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A Beginners' Guide to Modelling of Electric Double Layer under Equilibrium, Nonequilibrium and AC Conditions

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Lu-Lu Zhang^{is}, Chen-Kun Li², Jun Huang³

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Equilibrium, Nonequilibrium and AC Conditions

Lu-Lu-Zhang¹⁶, Chen-Kun Li³⁶, Jun Huang³⁶

(***I. School of Chemistry and Materials Science, Unierstity of Science a* **A Beginners' Guide to Modelling of Electric Double Layer under
Equilibrium, Nonequilibrium and AC Conditions

Lu-Lu Zhang^{ue}, Chen-Kun Li², Jun Huangⁿ

(***l. School of Chemistry and Marchia Scenec, Unitersity of Scie* **EQUIIIDFIUM CONDUMATE ANTISE ACCOLUMATE ANTISE ACCOLUMATE ANTISE A** L. School of Chemistry and Moterials Science, University of Science and Technology of China,

Hefei 230026, Anhui, People's Republice of China; 2. College of Chemistry and Chemical Engineering,

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3. Institute of Theoretical Chemistry, UIm **Abstract:** In electrochemistry, perhaps also in other time-honored scientific disciplines, knowledge labelled classical usually at-
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ste sets a stenchio from beginners, sepecially those pressured or temped to quickly am in tracts less attention from beginners, especially those possured or tempted to quickly jam into research forms that are labelled, not
always a phy, modern. In fact, it is a normal reaction in the barted or fustory and the atways aptly, modern. In fact, it is a normal reaction to the burden of history and the stress of today. Against this context, accessible unterails on classical knowledge are usefind, should some realize that taking a stap tubrials on classical knowledge are useful, should some realize that taking a step back could be the best way forward. This is the driving force of this arrive from the diversion firmed phopsicolearmical modelling of the

1 Introduction

1 Introduction
 1.1 What is An Electric Double Layer?
 2.1 An electrodensial cell has two electrodes separated by an electrolyte solution, as schematically shown in

Figure 1. The clectric potential difference betwe model for a simple Fi¹¹⁾. We ty na word the omission of supposedly 'trivial' information in the derivation of models, hoping that it and an an exercise to the wonderful garden of physical electrochemisty.
 Key words: e the access to the wonderful garden of physical electrochemisty.
 ords: electric double layer, equilibrium; nonequilibrium; decirochemical impediate spectroscopy
 Candition Park is An Electric Double Layer?
 Productio divide lawer of this arithmed at physiocelemical modelling of the electric (electric microsoftential) double layer (electric potential), we begin the potential and model the EDL under equilibrium, using firstly the orthod expeasion will a rudmmaliary introduction to key concepts of the LDL, bullowed by a breat miroductors of the methods. We then electrodes with the resultant electrodes in the resultant electrode-electroman model, and finall retune that the note of the most introduction as the parameteristic and the members of Vceller and the symmetro back and the members of the members of the members or the members or the members or the such of the members of manneous the statement of electrodechinial method in the statement of the section of several angular method of the distributed over a skin layer of several angular method for a simple lefth-
involvemental involvemental in tion and mathematical foundation of electrochemical impedance spectroscopy (EIS), and present a detailed derivation of an EIS

cond for a simple EDL. We try to avoid for onission of supposedly 'trivital' information in th

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 $\frac{\text{d} \ell \# (J. Electronchem.) 2022, 28(2), 2108471 (2 of 30)}{\text{d} \ell}$
the electrode surface via electrostatic interactions, as illustrated in Figure 1. In addition, the solvent molecules
adjust their orientation according to the strong the electrode surface via electrostatic interactions, as illustrated in Figure 1. In addition, the solvent molecules
adjust their orientation according to the strong electric field generated by the net surface charge. The **henomena occur in a non-electroochem.**) 2022, 28(2), 2108471 (2 of 30)
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dalust their orientation according to th function of the electrode surface via electrostatic interactions, as illustrated in Figure 1. In addition, the solvent molecules
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digitat their orientation according to the strong electric field generated by the net surface charge. These compled

phenomena occur in a non-electrometral region be electrode surface via electrode interaction, solution is considered in Figure 1. In addition, the solvent molecules
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adjust their orientation according to the strong electric field generated by the net surface charge. These coupled
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double layer (EDL).
Howevel are the electron of solution or reduction of solution species near
the electrode. T gion of a few nanometer (nm) thick, which is termed as the electric
the EEI, resulting in oxidation or reduction of solution species near
ends on the distributions of the electric potential, the concentrations
polarizatio In most cases, the electron flow many electrons are included in the decretis of the calculation or electrons are the electrons.
In most cases, the electron framsfer rate depends on the distributions of the electric potent In most cases, the electron flow can cross the EEI, resulting in oxidation or reduction of solution species near
the electrode. The electron transfer rate depends on the distributions of the electric potential, the concen the electrotic. The lectron translar rate depends on the distributions of the electrope inference. In expectrations of the distributions of the distributions of the subsection constrained properties of the EDL are importa reactant and product, and the deciever potarzation of the solvetion environment. Incretore, the structure
 2 Key Properties of the EDL are important factors influencing interfacial electron transfer reactions.
 2 Key P and properties of the EUL are mappetant tactors intuoneng intertacal electron transier reactions.

1.2 Key Properties of the EDL

The distributions of the clettric potential, the ion concentrations, and the solvent orient **1.2 Key Properties of the EDL**
The distributions of the cheric potential, the ion concentrations, and the solvent orientation in the EDL are
dictated by the excess surface charge density, denoted σ_{bc} . In an electroch The distributions of the electric potential, the ion concentrations, and the solvert orientation in the FDL are
dictated by the sceess surface charge density, denoted $\sigma_{\nu_{\alpha}}$ in an electrochemical cell, the two electr dictated by the excess surface charge density, denoted σ_{bb} . In an electrochemical cell, the two electrodes have σ_{bb} for same of the same magnitude but opposite signs, because the full cell must be clectronoutral. of the same magnitude but opposite signs, because the full cell must be electroneutral. σ_N can be varied as a function of $V_{\rm gal}$ or as long as a single electrode, considered decronde. The relation between σ_{M} and

EQUATE 1
 EQUATE 1 Electrochem.) 2022, 28(2), 2108471 (3 of 30)
 EQUATE 1 and towards more positive values.

For the case of $\phi_M - \phi_S = \chi$, as illustrated in Figure 2(B), the electric potential in whole electrol:

i For the case of $\phi_M - \phi_s = \chi$, as illustrated in Figure 2(B), the electric potential in whole electrolyte solution

EFor the case of $\phi_M - \phi_s = \chi$, as illustrated in Figure 2(B), the electric potential in whole electrolyte is $\# \&L^{\#}(J. \text{Electrochem.})$ 2022, 28(2), 2108471 (3 of 30)

fowards more positive values.

For the case of $\phi_M - \phi_S = \chi$, as illustrated in Figure 2(B), the electric potential in whole electrolyte solution

is zero as we hav the electrode surface, i.e., $\frac{d_1}{d_2}$ (*Leterrochem.*) 2022, 28(2), 2108471 (3 of 30)
towards more positive values.
For the case of $\phi_M - \phi_S = \chi$, as illustrated in Figure 2(B), the electric potential in whole electro $4 \frac{R \cancel{m}}{4}$ (*L Electrochem.*) 2022, 28(2), 2108471 (3 of 30)

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For the case of $\phi_M - \phi_S = \chi$, as illustrated in Figure 2(B), the electric potential in whole electrolyte solution

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For the case of $\phi_M - \phi_S = \chi$, as illustrated in Figure 2(B), the electric potential in whole electrolyte solution

is zero as we have set the potential reference in th $\frac{d}{dt}\left\{\frac{d}{dt}\left(f, \frac{d}{dt}\right) - 2(22, 28(2), 2108471 \cdot (3 \text{ of } 30)\right\}\right\}$

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For the case of $\phi_M - \phi_S = \chi$, as illustrated in Figure 2(B), the electric potential in whole electrolyte solution

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For the case of $\phi_M - \phi_S = \chi$, as illustrated in Figure 2(B), the electric potential in whole electrolyte solution

celectrode surface, i.e., $\sigma_M = 0$. Th the $\ell\ell\ell^2(L$ Electomehem.) 2022, 28(2), 2108471 (3 of 30)

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For the case of $\phi_{M} - \phi_{N} = \chi$, as illustrated in Figure 2(B), the electric potential in whole electrolyte solution

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s illustrated in Figure 2(B), the electric potential in whole electrolyte solution

ial reference in the bulk solution. There is no excess charge in the EDL or on

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C_{\rm dl} = \frac{\partial \sigma_{\rm M}}{\partial \phi_{\rm M}} \tag{1}
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Example 12
 Charged due to the particular charge transfer in the particular charge transfer and the particular of the particular of the particular of $\alpha_{\rm M}$ **of the particular of** $\alpha_{\rm M}$ **of the particular of \alpha_{\rm** d(*P^{*}*₂*t*</sup> *L kleetrochem*,) 2022, 28(2), 2108471 (3 of 30)

towards more positive values.

For the case of $\phi_{N} - \phi_{S} = \chi$, as illustrated in Figure 2(B), the electric potential in whole electrolyte solution
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For the case of $\phi_{\text{M}} - \phi_{\text{s}} = \chi$, as illustrated in Figure 2(B), the electric potential in whole electrolyte solution
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For the case of $\phi_M - \phi_S = \chi$, as illustrated in Figure 2(B), the electric potential in whole electrolyte solution

is zero as we have set the towards more positive values.
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For the case of $\phi_{N-1} - \phi_{N-2}$, as illustrated in Figure 2(1), the electric potential in whole electrolyte solution

is zero as we towards more positive values.

For the case of $\phi_{A} - \phi_{S} = \chi$, as illustrated in Figure 2(B), the electric potential in whole electrolyte solution

is zero as we have set the potential reference in the bulk solution. Th For the case of $\phi_M - \phi_S = \chi$, as illustrated in Figure 2(B), the cleartic potential in whole electrolyte solution
is zero as we have set the potential reference in the bulk solution. There is no excess charge in the EDL o is zero as we have set the potential reference in the bulk solution. There is no excess charge in the FDL or on
the electrode surface, i.e., $\sigma_M = 0$. This particular value of ϕ_0 is the *potential of zero* charge (pzc the electrode surface, i.e., $\sigma_{\alpha} = 0$. This particular value of ϕ_{α} is the potential of *zero* charge (px2)². For the case of $\phi_{\alpha} = \phi_{\alpha} > \chi$, shown in Figure 2(C), anions are accumulated and cations are dep $\phi_M - \phi_S > \chi$, shown in Figure 2(C), anions are accumulated and eations are depleted in the EDL, i.e., $\sigma_M > 0$.
Overall, the $\sigma_M - \phi_M$ relation shows a monotonically increasing trend for ordinary EDLs. From this relation, tim the differential double-layer expactiance C_{th} .
 $=\frac{\partial G_{th}}{\partial \phi_{tot}}$. (1)

For FDLs with chemisorption, the surface charging relation can be nonmonotonic. In Figure 2, we give such

example, where chemisorption occurs $C_{\text{d}} = \frac{\partial \sigma_{\text{M}}}{\partial \phi_{\text{M}}}$ (1)

For FDLs with chemisorption, the surface charging relation can be nonmonotonic. In Figure 2, we give such

an example, where chemisoption occurs in the high potential range. The chem $t_{\rm a} = \frac{1}{\partial \phi_{\rm at}}$

For EDLs with ehemisorption, the surface charging relation can be nonmonotonic. In Figure 2, we give such

for EDLs with electrochemics in the high potential range. The chemisorbates are usually p For EDLs with chemisorption, the surface charging relation can be nonmonotonic. In Figure 2, we give such
an example, where chemisspiton occurs in the high potential range. The charmisorbats are usually particly
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Then, we introduce EDL models u the supporting information.
The remaining parts of this paper are organized as follows. We first provide a brief history of the EDL theory.
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The remaining parts of this paper are organized as follows. We first provide a brief history of the EDL theory.

Then, we intr the Bikerman model that takes ion size effects into account, and finally a model that the BDL theory.
Then, we introduce EDL models under equilibrium conditions, including the Gouy-Chapman-Stern model, then
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Then remaining parts of this paper are organized as follows. We first provide a brief history of the EDL theory.
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The remaining parts of this paper are organized as follows. We first provide a brief history of the EDL modes
Then, we introduce EDL modes lander equilibrium conditions, including the Gouy-C if us supprovide interfaces due to its follows. We first provide a brich history of the EDL theory.
Then, we introduce EDL models under equilibrium conditions, including the Gouy-Chapman-Stern model, then
the Bikerman mod Then entraming plans or univ super a to upgarbe a so tonvisor, we mix power a lote massivy or the criterior.
Then, we initroduce EDL models under equilibrium conditions, including the Gouy-Chapman-Stern model that conside Then, we univore EDL moote that the electrode surface univorsal in the counterions in the Helmholtz plane (HP)⁹¹.
This vary memories of the electrode surface and the electrode surface and positive and positive in the su The alternation of the the diffuse and secure is the solution of the diffuse dotation of the HDL.

Afterwards, we present the basics of FIS, and demonstrate how to derive an FIS model from the nonequilibrium

EDL models.
 assummeter out size energy. Next, we derive independent in the three sizes in a grand potential of use Expansion Afterwards, we present the basis of EIS, and demonstrate how to derive an EIS model from the nonequilibric E EVARUATE THE STERN THE CONDUCTED THE CONSTRAINT IN THE STERN THE CONSTRAINT THE AND INTERFERIGAT AND MONET AND MONET AND MONET AND MONET AND MONET AND MANUSIAL USP IN THE STERN THE STERN THE STERN THE STERN THE STERN THE **EXECT THIS MOTH CONDIGATE THEOTY**
 2. A Brief History of the EDL Theory

A quantitative determination of the $\sigma_{x} = f(\phi_{y})$ relation requires a physicochemical model for the EDL. Figure

3 summarizes milestonons in the **A BIFIE HISTOTY OF THE EDLE THEOTY A** quantitative determination of the $\sigma_{\rm M} = f(\phi_0)$ relation requires a physicochemical model for the EDL. Figure A quantitative determination of the $\sigma_{\rm M} = f(\phi_0)$ relation of ED A quantitative determinion of the $\sigma_M = f(\phi_M)$ relation requires a physicochemicalle for the FDL. Figure

3 summarizes milestons in the volution of EDL modelling and simulations. Helmhot ED(379) viewed in

EDL as a planar 3 summarizes milestones in the colution of EDL modeling and simulations. Helmholtz (1879) viewed the EDL as a pharar plate capacitor with a constant double-layer capacitomec (G_a) and a linear potential distribution in t FIJ). as a planar plate capacitor with a constant double-layer capacitance (C_a) and a linear potentral distribution in the pace between two plates? FOR FIGRE from Hclmholtz who assumed a rigid lining up of conuntrions, G

the space between two plates⁵⁰. Different from Helmholtz who assumed a rigid Immig up of counterions, Giony
and Chapman considered the diffuse nature of counterions in the electrolyte solution in 1910^{n. a}, ten years b and Chapman consacterd the diffuse nature of countrions in the clectrolyte solution in 1910^{tos}; ten years be
component and Huckel. In the Gouy-Chapman model, the electric peotential and ion concentrations are governed
by Debye and Hinckel. In the Gouy-Chapman model, the electrolyte solution is vewed as a cloud of point in sectrom
bedded in a dielectric continuum. The Gouy-Chapman model is limited to overy dilute solutions are governed
by bedded an a delector continuum. The distributions of the electric potential and on concentrations are governed
by the poisson-Boltzman equation. The Gouy-Chapman model is limited to very ditter solutions at slighty
behape by the Poisson-Boltzmann equation. The Gouy-Chapman model is limited to very dittle solutions at sightly
the boshion-boltzmann counterion the point charge assumption. At highly charged interfaces or when
the apsi shifted charged interloss due to its bundation on the point charge assumption. At highly charged interlascs or when ϕ_{th} is shifted far away from the pz. the Gouy-Chapman model results in an amphysically high concentration of is shitted throws in the presence in the presencent in the presencent in the presencent in the magnitudis in the presence of the binser and the presence of the diffuse layer, denoted d_n becomes very small, leading to th counterions near the electrode surface. Under such scenarios, the gap between the electrode surface and the middleno of the diffuse layer, denoted d_n becomes very small, leading to the phenomenon of expacificy catastro-
 mighian of the diritities layer, denoted d_m , becomes very small, leading to the phenomenon of capacity catastro-
phe, namely, C_d grows toward infinity.
Stern removed this limitation by constraining the closest approac phe, namely, U_{α} grows toward unitsty.

Enter neurovel this limitation by constraining the closest approach of counterions to the Helmholtz plane (HP)³¹.

This way, regardless of the magnitude of surface charge dens Stern emrowed this limitation by constraining the closest approach of counterons to the lielmboliz plane the inter-
This way, regardless of the magnitude of surface charge density on the get into a leveling off region. Bi This way, regardless of the magnitude of surface charge density on the electrode, d_n has a lower limit, thus turn-
ing the canstrophic growth of G_a when ϕ_{ta} is shifted away from the pzc into a leveling off region. ing the canastrophite growth of U_{α} when ϕ_{α} is shitted away from the poe into a leveling of reguoin. Biferman, furthered the consideration of ion size in Stern's and Bikerman's treatments. Although d_{α} is co

Intributed the consideration of ton *size* elters thang a lattice-gas model¹⁹⁹. There is a delciate difference regarding the consideration of ion size in Stern's and Bikerman's treatments. Atthough d_0 is constrained hame calculated the differential capacitance of the inner layer (C_{HP}) as a function of $\sigma_{\text{M}}^{[13]}$. C_{HP} is asymmetric and ained in the Stern mod-

ained in the Stern mod-

t the HP and in the dif-

concentration at the HP

uently, in the Bikerman

unterion overcrowding,

citance profile is usual-

file is obtained, as d_0 al-

vided the HP the consideration of ton size in Shern is and Biderman's irredurented. Although d_6 is constrained in the Stern model, the Dissay-Boltzmann equation is inherited. This means hat the ion concentration at the HP and in th

电化学(*J. Electrochem.*) 2022, 28(2), 2108471 (5 of 30)

mamely, description of water dipoles at the IHP and description of metal elec-

year in 1958/59 in Britain and had a fruitful collaboration with Roger Parsons.

s exp

two new lines of EDL modelling, namely, description of water dipoles at the IHP and description of metal electrons, which are detailed below.

Grahame spent his sabbatical year in 1958/59 in Britain and had a fruitful col $\# \ell \# (L \n *Electrochem.*) 2022, 28(2), 2108471 (5 of 30)$
two new lines of EDL modelling, namely, description of water dipoles at the IHP and description of m
trons, which are detailed below.
Grahame spent his sabbatical year in (*Exectrochem.*) 2022, 28(2), 2108471 (5 of 30)

the UHP and description of metal elec-

ms, which are detailed below.

Grahame spent his sabbatical year in 1958/59 in Britain and had a fruitful collaboration with Roger P $\mathbb{R} \mathbb{R}^{\omega}$ (*L Electrochem.*) 2022, 28(2), 2108471 (5 of 30)
two new lines of EDL modelling, namely, description of water dipoles at the IHP and description of metal elec-
trons, which are detailed below.
Grahame **H**($R^{2\%}(L\text{ *Electrochem*}) 2022, 28(2), 2108471 (5 of 30)$
two new lines of EDL modelling, namely, description of water dipoles at the IHP and description of metal elec-
trons, which are detailed below.
Grahame spent his sabba **E***ft*²²(*L Electrochem.*) 2022, 28(2), 2108471 (5 of 30)
two new lines of EDL modelling, namely, description of water dipoles at the IHP and description of metal elec-
trons, which are detailed below.
Grahame spent ± 0.222 , $28(2)$, 2108471 (5 of 30)
two new lines of EDL modelling, namely, description of water dipoles at the IHP and description of metal elec-
trons, which are detailed below.
Grahame spent his sabbatical year in thers (*J. Electrochem.*) 2022, 28(2), 2108471 (5 of 30)
two new lines of EDL modelling, namely, description of water dipoles at the IHP and description of metal elec-
trons, which are detailed below.
Grahame spent his sa the *H*C² (*J. Electrochem.*) 2022, 28(2), 2108471 (5 of 30)
two new lines of EDL modelling, namely, description of water dipoles at the IHP and description of metal elec-
trons, which are detailed below.
Grahame spent **ELET THE MAY (Follow**) and the molecules may occupy the state of production of metal externation of metal electrons, which are detailed below.
This British are detailed below.
This British visit disseminated his experime **EXALUATE (Example at more polarized at more charged surface)**
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two new lines of EDL modelling, namely, description of water dipoles at the IHP and description of metal elec-
trons, which are detailed below.
This British vis $4E/4E$ *(Electroschern.*) 2022, 28(2), 2108471 (5 of 30)
two new lines of EDL modelling, namely, description of water dipoles at the IHP and description of metal elec-
trons, which are detailed below.
Grahame spent his s $\frac{41}{4}E_{\ell}^{*2}(L\text{Recone-ken}) 2022, 28(2), 2108471 (5 of 30)$
two new lines of EDL modelling, namely, description of water dipoles at the HIP and description of metal elec-
trons, which are detailed below.

Graham span has sab th $(2\frac{16}{7}(L\,Electrochehem, 2022, 28(2), 2108471 (S of 30))$
two new lines of FDL modelling, namely, description of water dipoles at the HFP and description of metal elec-
trons, which are detailed below.

Grahams spent his subshir Schmickler[18]. new lines of EDL modelling, namely, description of water dipoles at the IHP and description of metal elec-
orgalanme spent his subbatical lyear in 1958/59 in Britain and had a fruitful collaboration with Roger Parsons.
is Crons, which are detailed below.

Grahams spont his sabbathedal year in 1958/59 in Britain and had a fruitful collaboration with Roger Parsons.

Grahams spannia sabbathed his experimental findings among physicists at Camb Grahame spent his subbatical year in 1958/59 in Britain and had a fruitful collaboration with Roger Parsons.
This Briths visit disseminated his experimental findings among physicists at Cambridge. Wats-Tobin and Mot
tried This British visit disseminated his experimental findings among physicies at Cambridge. Watts-Tobin and Mott

tried to interpret the rise of C_{FP} for anodic polarizations and the hanny of C_{FP} at a ϕ_{e} sl tried to interpret the rise of C_{BP} for anodic polarizations and the hump of C_{BP} at a ϕ_{M} slightly positive to the precincually also concretorisal, pluasible causes including adsorbed hydroxy) ions, pote pze¹¹⁴. The former phenomenon had been controversial, plausible causes including adsorption of mercury ions,
specifiedly adsorbed hydroxy ions, potential varying distance between the OHP and the metal surface, among
orbe specifically adsorbed hydroxyl ions, potential varying distance between the OHP and the metal surface, smong
other⁵¹. The latter phenomenon is asserbed to the orientational polarization of interfacial water moleculess m others^[13]. The latter phenomenon is ascribed to the orientational polarization of interfacial water molecules, which was nittilally suggested by Worshard-Tooln⁻¹⁸. Watts-Tobin⁻⁸⁸. Watter-Tooln⁻¹⁹. Watter-Tooln⁻¹

was initially suggested by Grahame and latter modelled by Watts-Tobin¹⁹⁹. Watts-Tobin assumed that interfacial
vare moleculars may occupy two states (E-down or O-down). The basic idea is that interfaciel water molecules tionalize the metal and surface-charge dependence of $C_{\text{HP}}^{[17]}$. ther molecules may occupy two states (H-down or O-down). The basic idea is that interfacial water molecules

is more polarized at more charged surface, resulting in a decreased permittivity and lower C_{air} . Consequent are more polarized at more charged surface, resulting in a decreased permittivity and lower C_{inv} . Consequently, the thump of C_{inv} is locard at the pzc where the permittivity of water molecules is naximum. The de the hump of $C_{\rm IF}$ is located at the pzc where the permittivity of water molecules is maximum. The deviation of
the hump from he pzc observed in experiments is eased by the 'natural field' on the metal surface, namely, the hump from the pzc observed in experiments is caused by the 'natural field' on the metal surferee, smelley, met-
al electronic effects, which became a hot topic in 1980s^{[73}]. The Watts-Tobin model had been refined in al electronic effects, which became a hot topic in 1980s⁽¹³⁾. The Watts-Tobin model had been refined in several
counsiby considering more states of water and the hydrogen-bond network, sec a review by Guidelli and
Schmi

rounds by considering more states of water and the hydrogen-bond network, see a review by Guidelli and
Schmickle^{rta},
Trasatti's correlation between C_{HP} of simple sp metals taken at the pzc and the metal electronic Schmickler^{tin},

Teagelite with Grahame's data of $C_{\mu\nu}$ that gave the first hint of the importance of metal electronic effects,

Trasatti's correlation between $C_{\mu\nu}$ of simple sp metals taken at the pzc and the m Together with Grahame's data of $C_{\rm IP}$ that gave the first hint of the importance of metal electronic effects,
Trassiti's correlation between $C_{\rm HP}$ of simple sp metals taken at the pres and the metal electronic ansit Trasatti's correlation between C_{BF} of simple sp metals taken at the pze and the metal electron chearisy drove
theorists to explicitly consider the metal electronic effects^[19], In 1980s, Schmickler, Badiali, Korny theorists to explicitly consider the metal electronic effects¹⁰¹. In 1980s, Schmickler, Badiali, Komyshev and
their associates introduced the jellium model that that been vaidely used in the theory of metal surfaces to their associates introduced the jellium model that had been widely used in the theory of metal surfaces to the
BDL throw¹⁹⁸³. In the jellium model, the metal is treated as an inhomogeneous electron gas was described usi EDL theory¹²⁶²³⁾. In the jellium model, the metal is treated as an inhomogeneous electron gas situated against a
positive beckgroomd charge corresponding to metal caionic cores. The clettron gas was described using loca sitive background charge corresponding to metal cationic cores. The electron gas was described using local
is later replaced with pseudopotentials to consider metal specific behaviors. The jestitive background charge
late density approximations, such as the Thomas-Fermi-von Weizsücker theory¹⁵¹. The positive hackground charge
was later replaced with seudopotentials to consider metal specific behaviors. The jellium model is able to ra-
tr was later replaced with pseudopotentials to consider metal specific behaviors. The jellium model is able to ra-
tionalize the metal and surface-charge dependence of $C_{\text{tot}}^{(m)}$.
The next milestone in the EDL modelling i tionalize the metal and surface-charge dependence of $C_{\text{int}}^{[1]}$. The next milest DDL modelling is the work of Prices in the EDL modelling of Tries and the EDL modelling is the work of Price and Halley in 1995²⁴. They The next milestone in the FDL modelling is the work of Price and Halley in 1995²⁴. They adopted the Car-Pariollo method of combining molecular dynamics and density functional theory (DFT) to simulate the EDL Since then, rinello method of combining molecular dynamics and density functional theory (DFT) to simulate the FDL
formed at a cooper slob and water molecules. This work opened up a new direction in atomistic modelling of
the EDL. Si

 \mathcal{H}/L *Electrochem.*) 2022, 28(2), 2108471 (6 of 30)
theory for the electronic kinetic energy, a rudimentary kinetic energy density functional (KEDF), and the Dirac-
Wigner theory for the exchange-correlation function $\pm \frac{1}{2}$ (*L Electrochem.*) 2022, 28(2), 2108471 (6 of 30)
theory for the electronic kinetic energy, a rudimentary kinetic energy density functional (KEDF), and the Dirac-
Wigner theory for the exchange-correlation f $\exists (k \neq (J. Electrochem.) 2022, 28(2), 2108471 (6 of 30))$
theory for the electronic kinetic energy, a rudimentary kinetic energy density functional (KEDF), and the Dirac-
Wigner theory for the exchange-correlation functional, a rudimen **Example 10**
 Example 10 $\frac{4}{16}\left(\frac{1}{26}\right)^{22}$ (*L Electrochem.*) 2022, 28(2), 2108471 (6 of 30)
theory for the electronic kinetic energy, a nulmentary kinetic energy density functional (KEDF), and the Dirac-
Wigner theory for the exchange-co \pm *(E\\thetis)* . Electronic kinetic energy, a rudimentary kinetic energy density functional (KEDF), and the Dirac-Wigner theory for the exchange-correlator functional a rudimentary local density approximation. As for tential. $\oplus \&E \nrightarrow \&E$
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 $\cong \&E \nrightarrow \&E \nrightarrow \&E \nrightarrow \&E \nrightarrow \&E \nrightarrow \&E \n$ $\mathbf{E}E \cong (J. Electronen) 2022, 28(2), 2108471 (6 of 30)$
theory for the electronic kinetic energy, a rudimentary kinetic energy density functional (KEDF), and the Dirac-
Wigner theory for the exchange-correlation functional, a rudim th $\&E^{\omega}(L\&Rlectmchem, 2022, 28(2), 2108471 (6.6730)$
cory for the electronic kinetic energy, a rudimentary kinetic energy density functional (KEDF), and the Dirac-
igner theory for the exchange-correlation functional, a rudim **ELET (E. Klectronchen, 2022, 28(2), 2108471 (6 of 31)**
 **Chargent Theory for the electronic kinetic energy, a rudimentary kinetic energy density functional (KEDF), and the Dirac-

Wigner theory for the exchange-correlati EXAMPLE 12** and the diffusion of the electronic since the electronic subfigure in the diffusion of the Dirac-Wigner theory for the exchange-correlation functional, a rudimentary local density approximation. As for the el **usually the radius of a hydratic meantal (i)** The PF equation describes the distributions of the electric potential and the ion-concentrations of $\Psi(\xi) = -\sum_{i=1}^N E_i$

Wigner theory for the exchange-correlation function **The PE extraceleran**, 2022, 28(2), 2108471 (6.6130)

The PE electronic kinetic energy, a radiometrary kinetic energy density functional (KEDF), and the Dirac-

electrolyte solution, Huang developed a statistical field th **the UP of the UP of the UP** of *Rectrochem.*) 2022, 28(2), 2108471 (6 of 30)

theory for the electronic kinetic energy, a rudimentary kinetic energy density functional (KEDF), and the Dirac-Wigner theory for the exchange is the section of the controllation interior and the plane and the plane and the electric permittivity of the electric potential functional of the FDL is obtained. Variational analysis of this functional yields a grand-ca executory solution, than give texpolarisation incidental into the bulk solution, and ion-specific interactions with the metal^{ta}¹¹. Combined, a hybrid density-potential figrand potential functional of the EDL is obtain per a statustar lear undary considering asymmetric steric enects, solvential functional for the iDL is obtained. Variational analysis of this functional yields a grand-canoni-
Euler-Lagrange equations in terms of the elec the concentrational for the
elds a grand-canoni-
and the electric po-
potential distributes
in in the diffuse layer
lectrode to the HP is
trations in the elec-
(2)
cd to the electric po-
the concentration of
(3)
e temperat 电化学(*J. Electrochem.*) 2022, 28(2), 2108471 (6 of 30)
c energy, a rudimentary kinetic energy density functional (KEDF), and the Dirac-
ge-correlation functional, a rudimentary local density approximation. As for the
velop

ianziation, and orientation with matted the sultime increases when the discussion of the figure and potential functional of the EDL is obtained. Variational analysis of this functional yields a grand-canonical EDL model d in the electrode to the HP, and is described by Poisson-Boltzmann (PB) equation in the diffuse layer

diffusion layer as shown in the third subfigure in Figure 3. The distance from the electrode to the HP is

causa to me **ilibrium Models**
 iv. Chapman-Stern Model

avy-Chapman-Stern (GCS) model is a classical toy moisel of the EDL. The electric potential distributes

om the electrode to the HP, and is described by Poisson-Boltzmann (PB) **3 Equividential monomisms Stern Models**
 3.1 Gouty-Chapman-Stern Model
 3.1 Gouty-Chapman-Stern Model
 3.1 Gouty-Chapman-Stern Model
 5.1 Gouty-Chapman-Stern Model
 5.1 Gouty-Chapman-Stern Model
 5.1 Counce-
 For the concentration of the HP, and is described by Poisson-Boltzmann (PB) equation in the diffuse layer
diffusion layer as shown in the third subfigure in Figure 3. The distance from the electrode to the HP is
Bequation

$$
\nabla (\epsilon_{s} \nabla \phi) = -\sum_{i} z_{i} F c_{i}
$$
 (2)

where ϵ_s is the dielectric permittivity of the bulk solution, ϕ the electric potential referenced to the electric po-

$$
c_i = c_i^{\text{log}} \exp\left(-\frac{z_i F}{RT} \phi\right)
$$
 (3)

where c_i ^b is the concentration of ion i in the bulk solution, R the gas constant, T the absolute temperature. For a

$$
\frac{\partial^2 \phi}{\partial x^2} = -\frac{Fc^b}{\epsilon_s} \left(\exp\left(-\frac{F\phi}{RT}\right) - \exp\left(\frac{F\phi}{RT}\right) \right) \tag{4}
$$

where c^b the concentration of total anions (cations) in the bulk solution. The dimensionless form of the PB equa-

$$
\text{# } \mathcal{U} \neq (J. \text{ Electrochem.}) 2022, 28(2), 2108471 (7 of 30)
$$
\n
$$
\frac{\partial^2 U}{\partial X^2} = \sinh(U) \tag{5}
$$
\nwith the dimensionless quantities, $U = F\phi/RT$, $X = x/\lambda_D$, and the Debye length $\lambda_D = \sqrt{RT\epsilon/2F^2c^b}$. Note that the dielectric permittivity depends on the local density of solvent molecules and the local electric field. In an aque-

 $\frac{1}{2}$ = sinh(*U*) (5)

¹/₂ = sinh(*U*) (5)

the dimensionless quantities, *U* = *Fφ/RT*, *X* = *x*/λ_D, and the Debye length λ_D = $\sqrt{RT\epsilon/2F^2c^5}$. Note that the lectric permittivity depends on the local den $\frac{\partial^2 U}{\partial X^2}$ = sinh(*U*) (5)
 $\frac{\partial^2 U}{\partial X^2}$ = sinh(*U*) (5)

with the dimensionless quantities, *U* = *Fψ/RT*, *X* = *x*/λ_D, and the Debye length λ_D = $\sqrt{RT_{\epsilon}/2F_{\epsilon}^{n}}$. Note that the

dielectric permittivi $\sqrt{RT \epsilon}/2F^2c^6$. Note that the (5)

. Note that the

d. In an aque-

to $78.5\epsilon_0$ in the

the HP. (i) $\frac{\partial^2 U}{\partial X^2}$ = sinh(*U*) (5)
 $\frac{\partial^2 U}{\partial X^2}$ = sinh(*U*) (5)

with the dimensionless quantities, $U = F\phi/RT$, $X = x/\lambda_D$, and the Debye length $\lambda_D = \sqrt{RT\epsilon/2F^2c^D}$. Note that the dielectric permittivity depends on $\frac{\partial^2 U}{\partial X^2}$ = sinh(*U*) (5)
 $\frac{\partial^2 U}{\partial X^2}$ = sinh(*U*) (5)

with the dimensionless quantities, $U = F\phi/RT$, $X = x/\lambda_D$, and the Debye length $\lambda_D = \sqrt{RT\epsilon/2F_e^2c^b}$. Note that the

dielectric permittivity depends on th $\frac{\partial^2 U}{\partial X^2}$ = sinh(*U*) (5)

with the dimensionless quantities, $U = F\phi/RT$, $X = x/\lambda_D$, and the Debye length $\lambda_D = \sqrt{RT\epsilon/2Fe^D}$. Note that the

dielectric permittivity depends on the local density of solvent molecules **EVALUATE EXAMORE 19.1302.** 28(2), 2108471 (7 of 30)
 $\frac{U}{V^2}$ = sinh(*U*) (5)

the dimensionless quantities, $U = F\phi/RT$, $X = x/\lambda_D$, and the Debye length $\lambda_D = \sqrt{RT\epsilon/2F^*c^*}$. Note that the

electric permittivity depend **EVACATE (EXAMPLE 1000** EVACATE 1 (1 of 30)
 $\frac{\partial^2 U}{\partial X^2}$ = sinh(*U*) (5)
 $\frac{\partial^2 U}{\partial X^2}$ = sinh(*U*) (5)

With the dimensionless quantities, $U = F\phi / RT$, $X = x/\lambda_D$, and the Debye length $\lambda_D = \sqrt{RT\epsilon/2Fc^b}$. Note that $\frac{\partial^2 U}{\partial X^2}$ = sinh(U) (5)

We $\mathcal{H}(L)$ Electrochem.) 2022, 28(2), 2108471 (7 of 30) (5)

We the dimensionless quantities, $U = F\phi/RT$, $X = x/\Delta_0$ and the Debye length $\lambda_0 = \sqrt{RT\epsilon_2 T^2e^{x_0}}$. Note that the

dielectri $\frac{\partial^2 U}{\partial X^2}$ = sinh(*U*) (5)
 $\frac{\partial^2 U}{\partial X^2}$ = sinh(*U*) (6)
 $\frac{\partial^2 U}{\partial X^2}$ = sinh(*U*) (6)

(6)

where dimensionless quantities, $U = F_0 b / RT$, $X = x / \lambda_D$, and the Debye length $\lambda_D = \sqrt{R T \epsilon / 2F_C^2}$. Note that the **EVALUATE (DEVALUATE ACT ALT CONSERVADE ACT ACTS)** (5)
 $\frac{\partial^2 U}{\partial \lambda^2}$ = sinh(*U*) (8)

(6)

with the dimensionless quantities, $U = F\phi/RT$, $X = x/\lambda_n$, and the Debye length $\lambda_n = \sqrt{RT\epsilon/2Fe^b}$. Note that the

with diction $\frac{d\Phi}{dt} = \sinh(t)$ (5)
 $\frac{\partial^2 U}{\partial \lambda^2} = \sinh(t)$ (5)
 $\frac{\partial^2 U}{\partial \lambda^2} = \sinh(t)$ (6)

We the dimensionless quantities, $U = F\phi/RT$, $X = x/\lambda_0$, and the Debye length $\lambda_0 = \sqrt{RT\epsilon/2}Fe^{\lambda_0}$. Note that the

widthe electric permitt $\frac{\partial^2 U}{\partial X^2} = \sinh(t)$ (5)
 $\frac{\partial^2 U}{\partial X^2} = \sinh(t)$ (5)

(5)
 $\frac{\partial^2 U}{\partial X^2} = \sinh(t)$ (6)

(6)

which dimensionless quantities, $U = F\phi/RT$, $X = x/\lambda_D$, and the Dobye length $\lambda_D = \sqrt{RT\epsilon/DFc^F}$. Note that the

dielectric permitt $\frac{\partial^2 U}{\partial X^2} = \sinh(U)$ (5)
 $\frac{\partial^2 U}{\partial X^2} = \sinh(U)$ (5)

with the dimensionless quantities, $U = F\phi/RT$, $X = x/\lambda_0$, and the Debye length $\lambda_0 = \sqrt{RT\epsilon/2F\epsilon_0}$. Note that the

dielectric permittivity depends on the local dens

$$
U(\lambda = 0) = U_{HP} \tag{6}
$$

where
$$
X = 0
$$
 represents the left boundary at the HP, and $X = \infty$ is the right boundary in the bulk solution. $\phi_{HP}^{[4]}$
(dimensional quantity of U_{tm}) can be calculated from the electrode side by.

$$
\phi_{HP} = \phi_M - \phi_{pzc} + \left(\frac{\partial \phi}{\partial x}\right)_{x=0^+} \frac{\epsilon_{s}}{\epsilon_{HP}} \delta_{HP}
$$
\n(8)

电化学(*J. Electrochem.*) 2022, 28(2), 2108471 (8 of 30)
vely. The coefficient $\epsilon/\epsilon_{\text{HP}}$ is resultant from the following equality in terms of sur-
trode surface,
 $\sum_{x=0}^{1}$ (9)

$$
\pm (k \frac{3\pi}{2} (J. Electrochem.) 2022, 28(2), 2108471 (8 of 30))
$$
\nelectrode and the HP, respectively. The coefficient ϵ/ϵ_{HP} is resultant from the following equality in terms of surface charge density on the electrode surface,
\n
$$
\sigma_M = -\epsilon_s \left(\frac{\partial \phi}{\partial x}\right)_{x=0} = -\epsilon_{HP} \left(\frac{\partial \phi}{\partial x}\right)_{x=0} = -\epsilon_{HP} \left(\frac{\partial \phi}{\partial x}\right)_{x=0} \tag{9}
$$
\nSolving Eq. (5) in the following steps,
\n
$$
2 \frac{\partial^2 U}{\partial X^2} \frac{\partial U}{\partial X} = 2 \sinh(U) \frac{\partial U}{\partial X}
$$
\n
$$
d\left(\frac{\partial U}{\partial X}\right)^2 = d(2 \cosh U) \tag{11}
$$
\n
$$
\left(\frac{\partial U}{\partial X}\right)_{x=0}^2 = \left(2 \sinh\left(\frac{U_{HP}}{2}\right)\right)^2 \tag{12}
$$

$$
2\frac{\partial^2 U}{\partial X^2} \frac{\partial U}{\partial X} = 2\sinh(U)\frac{\partial U}{\partial X}
$$
 (10)

$$
d\left(\frac{\partial U}{\partial X}\right)^2 = d(2\cosh U) \tag{11}
$$

$$
\frac{d_0^2 E^{\frac{2\alpha}{2}}(L \t\t\tE \text{leterrochem.}) 2022, 28(2), 2108471 (8 of 30)
$$
\n
$$
\frac{d_0^2 E^{\frac{2\alpha}{2}}(L \t\t\tE \text{leterrochem.}) 2022, 28(2), 2108471 (8 of 30)
$$
\n
$$
\sigma_M = -\epsilon_i \left(\frac{\partial \phi}{\partial x}\right)_{x=0} = -\epsilon_{\text{inf}} \left(\frac{\partial \phi}{\partial x}\right)_{x=0}.
$$
\nSolving Eq. (5) in the following steps,\n
$$
2\frac{\partial^2 U}{\partial X^2} \frac{\partial U}{\partial X} = 2\sinh(U) \frac{\partial U}{\partial X}.
$$
\n
$$
2\frac{\partial^2 U}{\partial X^2} \frac{\partial U}{\partial X} = 2\sinh(U) \frac{\partial U}{\partial X}.
$$
\n
$$
\left(\frac{\partial U}{\partial X}\right)_{x=0} = 2\sinh\left(\frac{U_{\text{tr}}}{2}\right)_{x=0}.
$$
\n
$$
\left(\frac{\partial U}{\partial X}\right)_{x=0} = 2\sinh\left(\frac{U_{\text{tr}}}{2}\right)_{x=0}.
$$
\n
$$
\left(\frac{\partial U}{\partial X}\right)_{x=0} = \left(2\sinh\left(\frac{U_{\text{tr}}}{2}\right)\right)^2.
$$
\n
$$
\text{We obtain the relationship between the surface charge density and the electric potential at the HP,}
$$
\n
$$
\sigma_M = -\int (c_+ - c_-)F\mathrm{d}x = -\epsilon_x \left(\frac{\partial \phi}{\partial x}\right)_{x=0} = \frac{2\epsilon_x RT}{R_0}\sinh\left(\frac{P_0V_{\text{tr}}}{2RT}\right) \qquad (13)
$$
\n
$$
\text{Byp4c is a convenient built-in tool in Matlab for solving boundary value problems described as ordinary differential equations. In accord with the syntax of this tool, Eq. (5) is rewritten as,\n
$$
\frac{\partial U}{\partial X} = \sinh(U)
$$
\n
$$
\frac{\partial Y}{\partial X} = \sinh(U)
$$
\n
$$
\frac{\partial Y}{\partial X} = \sinh(U)
$$
\n
$$
\text{where } Y = \frac{F\lambda_D}{RT
$$
$$

$$
\sigma_{\rm M} = -\int (c_{+} - c_{-})F dx = -\epsilon_{\rm s} \left(\frac{\partial \phi}{\partial x}\right)_{x=0^{+}} = \frac{2\epsilon_{\rm s}RT}{F\lambda_{\rm D}} \sinh \left(\frac{F\phi_{\rm HP}}{2RT}\right)
$$
(13)

$$
\frac{\partial U}{\partial X} = Y \tag{14}
$$

$$
\frac{\partial Y}{\partial X} = \sinh(U) \tag{15}
$$

where $Y = \frac{F\lambda_D}{RT} \frac{\partial \phi}{\partial x}$ is the dimensionless electric field strength. $\frac{\partial \phi}{\partial r}$ is the dimensionless electric field strength. ∂x is the dimensionless electric field

is the dimensionless electric field strength. Figure (3) $\frac{1}{10}$ and (1) $\frac{1}{100}$ (1) the two moves seeps,

Figure 4 (2cosh *l*) (1) (1)
 $\frac{\partial U}{\partial X}$ = 2sinh(*I*) $\frac{\partial U}{\partial X}$ = 2sinh($\frac{1}{2}$ = $\left(\frac{1}{2}$ = $\left(\frac{1}{2}$ = $\left(\frac{1}{2}\right)^2\right)$ = $\left(\frac{1}{2}$ = $\$ $2\frac{\Delta}{\Delta X^2} \frac{\partial \Delta Y}{\partial X} = 2\sinh(U) \frac{\partial \Delta Y}{\partial X}$ (10)
 $\left(\frac{\partial U}{\partial X}\right)^2 = d(2\cosh U)$ (11)
 $\left(\frac{\partial U}{\partial X}\right)^2 = \frac{1}{\sqrt{2}} \left(2\sinh\left(\frac{U_{\text{rms}}}{2\mu}\right)\right)^2$ (12)
 $\sigma_{\text{M}} = -\int (c - c)F dx = -\epsilon, \left(\frac{\partial \phi}{\partial x}\right)_{x=0} = \frac{2\epsilon_1 RT}{P\Delta_0} \sinh\left(\frac{P$ (1) $\frac{\partial U}{\partial X}$ $\Big|^{2} = d(2\cosh U)$ (12)
 $\left(\frac{\partial U}{\partial X}\right)_{Y=0}^{2} = \left(2\sinh\left(\frac{U_{\text{IR}}}{2}\right)\right)^{2}$ (12)

we obtain the relationship between the surface charge density and the electric potential at the HP,
 $\sigma_{\text{M}} = -\int (c_1 -$ (1)
 $\left(\frac{\partial U}{\partial X}\right)_{x=0}^{x=1} = \left(\frac{2\sinh\left(\frac{U_{\text{pp}}}{2}\right)}{2\sin\left(\frac{1}{2}\right)}\right)^{3}$ (12)

We obtain the relationship between the surface charge density and the electric potential at the HP,
 $\sigma_{\text{M}} = -\int (c, -c)F\mathrm{d}x = -\epsilon \left(\frac$ $\left(\frac{\partial U}{\partial X}\right)_{x-x^2} = \left(2\sinh\left(\frac{U_{\text{p}}}{2}\right)\right)$
 $\cos\theta \sin \theta$ the relationship between the surface charge density and the electric potential at the 1IP,
 $\sigma_{\text{N}} = -\int (c_x - c_x)^p dx = -e_x \left(\frac{\partial \phi}{\partial x}\right)_{x-x^2} = \frac{2e_x RT}{2RT} \sinh\left(\$

thentificant et ϕ_{p} .

A simple calculation can illustrate the failure of the GCS model in extreme cases. According to Eq.(3), $c_i = c_i^b$

exp (-z,*Fφ/RT*), we obtain $c_i = 8.18 \times 10^{16}$ mol·m⁻³, when $\phi = -1$ V, exp (-ziF准/RT), we obtain ci = 8.18 ^伊 ¹⁰¹⁶ mol窑m-³) 2022, 28(2), 2108471 (9 of 30)

GCS model in extreme cases. According to Eq.(3), $c_i = c_i^b$,

, when $\phi = -1$ V, $z_i = 1$, $c_i^b = 1$ mol·m⁻³ and $T = 298$ K.
 $\times 10^{-35}$ cm³. However, even for the smallest bare cation, to Eq.(3), $c_i = c_i^b$
and $T = 298$ K.
lest bare cation,
msider the finite E(E#Consequently, and the finite of the GCS model in extreme cases. According to Eq.(3), $c_i = c_i^*$

exp ($- z_i F \phi / RT$), we obtain $c_i = 8.18 \times 10^{16}$ mol·m⁻³, when $\phi = -1$ V, $z_i = 1$, $c_i^* = 1$ mol·m⁻³ and $T = 298$ K. 2108471 (9 of 30)

in extreme cases. According to Eq.(3), $c_i = c_i^b$

-1 V, $z_i = 1$, $c_i^b = 1$ mol·m⁻³ and $T = 298$ K.
 \therefore However, even for the smallest bare cation,
 $s_i^{[45]}$. Thus, it is necessary to consider the H⁺, the volume is approximately, $d_{\mu^*}^3 \approx (0.56 \text{ Å})^3 = 1.76 \times 10^{-25} \text{ cm}^{3[45]}$. Thus, it the velocity *H*(*E Electrochem.*) 2022, 28(2), 2108471 (9 of 30)

inimum at φ_{px}.

A simple calculation can illustrate the failure of the GCS model in extreme cases. According
 $P(-z_0F\phi/RT)$, we obtain $c_1 = 8.18 \times$ $\mathbb{R}^{\#}(J. Electrochem.)$ 2022, 28(2), 2108471 (9 of 30)

e the failure of the GCS model in extreme cases. According to Eq.(3), $c_i = c_i^b$

8 × 10¹⁶ mol·m⁻³, when $\phi = -1 \text{ V}, z_i = 1, c_i^b = 1 \text{ mol} \cdot \text{m}^{-3}$ and $T = 298 \text{ K}$.

a **EVATE THE EXECT THE EXECT AND THE EXECT AND THE EVALUATION OF SUPPOSET ARE REFORM IN A SIMPLE CASE OF** $(-z_i F \phi / RT)$ **, we obtain** $c_i = 8.18 \times 10^{16}$ **mol m⁻³, when** $\phi = -1$ **V,** $z_i = 1$ **,** $c_i^b = 1$ **mol · m⁻³ and** $T =$ **Conseque EVALUATE (EXECUTE 1902)**
 EVALUATE 1902
 EVALUATE 1903
 EVALUA EVACTE 1942, Bikerman realized the limitations of neglecting ion size in the dCS model in extreme cases. According to Eq.(3), $c_i = c_i^h$ **

p (** $-zF\phi/RT$ **), we obtain** $c_i = 8.18 \times 10^{16}$ **mol·m⁻³, when** $\phi = -1 \text{ V}$ **,** $z_i = 1$ **,** the *θ*_{*P*ec}.
 el, *θ*_{*Pec*}.
 el, *c_a* (*-z_iPb*/*RT*), we obtain c_i = 8.18 × 10^{*m*} mod · m⁻₃ when φ = −1 V, *z*_i = 1, *e*¹ = 1 mod · m⁻² and *T* = 298 K.

Exp (*-z_iPb/RT*), we obtain c_i the BPB model man illustrate the finiture of the GCS model in extreme cases. According to Eq.(3), $c_i = c_i$
A simple calculation can illustrate the finiture of the GCS model in extreme cases. According to Eq.(3), $c_i = c_i$
ex **EVALUATE MODE THE BEST MONET (SOLUTE THE SOLUTE SOLUTE AS A simple calculation can illustrate the finilure of the GCS model in extreme cases. According to Eq.(3),** $c_i = c_i^{\lambda}$ **as imple calculation can illustrate the fini** $\pm i(k\#(J. \text{ *Electrochem.*}) 2022, 28(2), 2108471 (9 of 30)$

inimum at ϕ_{pe} .

A simple calculation can illustrate the failure of the GCS model in extreme cas

p (-z,F¢/RT), we obtain $c_i = 8.18 \times 10^{16} \text{ mol} \cdot \text{m}^{-3}$, whe **is the first the definition** and illustrate the finiture of the GCS model in extreme cases. According to Eq.(3), $c_i = c_i^*$

Ray, we obtain $c_i = 8.18 \times 10^{16}$ mol \cdot m⁻³, when $\phi = -1$ V, $z_i = 1$, $c_i^* = 1$ mol \cdot m⁻ besons. According to Eq.(3), $c_i = c_i^b$
 $\frac{b}{i} = 1 \text{ mol} \cdot \text{m}^{-3}$ and $T = 298 \text{ K}$.

en for the smallest bare cation,

necessary to consider the finite

odel and developed a new mod-

n contrast with the GCS model,

e **EVATE 10** the the set of the finite of the finite of the set of the difference μ_i^2 is the elementary of \bar{L}_i^2 in \bar{L}_i^2 in \bar{L}_i^2 in the set of the set of the GCS model in extreme cas exp ($-z_iF\phi/RT$), w at ϕ_{iso} .

at ϕ_{iso} .

le calculation can illustrate the failure of the GCS model in extreme cases. According to Eq.(3), $c_i = c_i^*$
 ϕ/RT , we obtain $c_i = 8.18 \times 10^{16}$ mol·m⁻³, when $\phi = -1$ V, $z_i = 1$, $c_i^* =$ minimum at $\phi_{p\rightarrow}$

A simple calculation can illustrate the failure of the GCS model in extreme cases. According to Fq.(3), $c_1 = c_1^b$

exp $(-s_1F\phi/HT)$, we obtain $c_1 = 8.18 \times 10^{16}$ mol ·m⁻³, when $\phi = -1$ V, $z_i =$ 电化学(*J. Electrochem.*) 2022, 28(2), 2108471 (9 of 30)

rate the failure of the GCS model in extreme cases. According to Eq.(3), $c_i = c_i^b$

8.18 × 10¹⁶ mol·m⁻³, when $\phi = -1$ V, $z_i = 1$, $c_i^b = 1$ mol·m⁻³ and $T = 298$

 d_1^3 , where d_1 is the lattice size. The maximum particle number density is $n_t = d_1^{-3}$. The electrochemical potential

$$
\bar{\mu}_i = \mu_i^0 + z_i e_0 \phi + k_\text{B} T \ln \frac{d_i^3 n_i}{1 - d_i^3 \sum_i n_i} \tag{16}
$$

where μ_i^0 is the chemical potential under standard conditions, e_0 the elementary charge, ϕ the electric potential treme cases. According to Eq.(3), $c_i = c_i^b$
 $z_i = 1$, $c_i^b = 1$ mol·m⁻³ and $T = 298$ K.

wever, even for the smallest bare cation,

Thus, it is necessary to consider the finite

e GCS model and developed a new mod-
 $5^{$ d_t^3 the number density of solvent molecules. For a monovalent electrolyte solution, we have $n_t^0 = n_t^0 = n_t^0$, with S simple calculation can illustrate the failure of the GCS model in extreme cases. According to Fa(3), $c_i = c_i^P$, $(-z_i F_0)/T_i$, we obtain $c_i = 8.18 \times 10^{16}$ mol -m³, when $\phi = -1$ V, $z_i = 1$, $c_i^P = 1$ mol -m³ and $T =$ $c_i = c_i^b$
98 K.
aation,
finite
with the state of tential
(16)
tential
 $\sum_i n_i$)/
with
ectro-
(17) n^b the number density of total anions (c $p(-xF\phi/RT)$, we obtain $e_i = 8.18 \times 10^{16}$ mol \cdot m², when $\phi = -1$ V, $z_i = 1$, $e_i^2 = 1$ mol \cdot m² and $T = 298$ K.

the volume is approximately, $d_{\text{th}}z^2 \approx (0.56 \text{ Å})^2 = 1.76 \times 10^{26} \text{ cm}^3$. Thus, it is necess Consequently, each cation occupies a volume of 2.03 × 10⁻³ cm². However, even for the smallest bare cation, 11; the volume is approximately, $d_{\kappa}t^3 \approx (0.56 \text{ Å})^2 = 1.76 \times 10^{-8} \text{ cm}^{3.08}$. Thus, it is necessary to 3.2 **Symmetric Bikerman Model**

In 1942, Bikerman realized the imitations of neglecting ion size in the GCS model and developed a new mod-

In 1942, Bikerman realized the limitations of neglecting ion size in the GCS mode lled Bikerman-Poisson-Boltzmann (BPB) model, as shown in Figure 5^{[10,40}]. In cont

PB model presents a consistent treatment of the finite size of ions both at the HP a

ce BPB model treats the electrolyte solution using the BPB model presents a consistent treatment of the finite size of ions both at the HP and in the diffuse layer.

The BBB model teats the electrolyte solution using the lattice-gas approach. Each ion occupies a volume of size of ions both at the HP and in the diffuse layer.

lattice-gas approach. Each ion occupies a volume of

ber density is $n_t = d_t^{-3}$. The electrochemical potential

(16)

ns, e_0 the elementary charge, ϕ the electri The BPB model treats the electrolyte solution using the lattice-gas approach. Fach ion occupies a volume of

where d_i is the lattice size. The maximum particle number density is $n_i = d$ ². The electrochemical potential
 d_i , where d_i , is the lattice size. The maximum particle number density is $n_i = d_i$. The el

for ion *i* reads,
 $\overline{\mu}_i = \mu_i^0 + z e_0 \phi + k_B T \ln \frac{d_i^3 n_i}{1 - d_i^3 \sum_i n_i}$

where μ_i^0 is the chemical potential under standard s,
 $\phi + k_B$ $T \ln \frac{d_i^2 n_i}{1 - d_i^2 \sum_i n_i}$

the chemical potential under standard conditions, e_0 the elementary charge, ϕ the

that in the bulk solution, ϕ_s , k_B the Boltzmann constant, n_i the number density of i $\bar{u}_s = \mu_s^n + z \rho_s \phi + k_B \text{ Th} \frac{d_s^2 h_s}{1 - \mu_s^2 \sum \mu_s}$ (16)

where μ_s^0 is the chemical potential under standard conditions, e_s the elementary charge, ϕ the electric potential

referenced to that in the bulk solution ⁹ is the chemical potential under standard conditions, e_o the elementary charge, ϕ
ed to that in the bulk solution, $\phi_{\rm s} k_{\rm B}$ the Boltzmann constant, *n*, the number density
umber density of solvent molecules referenced to that in the bulk solution, $\phi_b k_0$ the Boltzmann constant, n_i the number density of ion i , $(1-d_i^T \sum_i n_i)^i$
 d_i^2 the number density of solvent molecules. For a monovalent electrolyte solution, we have

$$
\bar{\mu}_{i} = \mu_{i}^{0} + z_{i}e_{0}\phi + k_{B}T \ln \frac{d_{t}^{3}n_{i}}{1 - d_{t}^{3}\sum_{i}n_{i}} = \mu_{i}^{0} + k_{B}T \ln \frac{d_{t}^{3}n^{b}}{1 - 2d_{t}^{3}n^{b}}
$$
(17)

$$
n_i = \frac{n^{\text{b}} \exp(-z_i e_0 \phi / k_B T)}{1 + 2v \sinh^2(z_i e_0 \phi / 2k_B T)}
$$
(18)

 n^b . The GCS model assumes $v = 0$.

$$
\nabla (\epsilon_{\rm s} \nabla \phi) = \frac{2n^{\rm b}z_i e_0 \sinh(z_i e_0 \phi / k_{\rm B} T)}{1 + 2v \sinh^2(z_i e_0 \phi / 2k_{\rm B} T)}
$$
(19)

$$
\frac{\partial^2 U}{\partial X^2} = \frac{\sinh U}{1 + 2v \sinh^2(U/2)}\tag{20}
$$

$$
\sigma_{\rm M} = -\int (n_{+} - n_{-})e_{0} \, \mathrm{d}x = -\,\epsilon_{\rm s} \left(\frac{\partial \Phi}{\partial x}\right)_{x=0^{+}} \tag{21}
$$

al anions (cations) in the bulk solution. Under equilibrium conditions, the electro-
is uniform in the whole EDL,
 $\frac{n_i}{n_i} = \mu_i^0 + k_B T \ln \frac{d_i^2 n^b}{1 - 2d_i^2 n^b}$ (17)
 $\sum_{i=1}^n m_i = \mu_i^0 + k_B T \ln \frac{d_i^2 n^b}{1 - 2d_i^2 n^b}$ (17)
 The ^耶bvp4c^爷 function in Matlab is employed to solve Eq. (20) closed with the boundary conditions ex- $\mu_r = \mu_j^{0.1} \cdot z_e d_b + k_0 T \ln \frac{d_i \hbar_i}{1-d_i \sum_i \mu_i} = \mu_i^{0.1} + k_0 T \ln \frac{d_i \hbar^b}{1-2d_i \hbar^b}$ (17)

The number density of ion is obtained as,
 $n_i = \frac{\hbar^2 \exp(-z_i e_0 \phi b_i \mu_i)}{1 + 2v \sinh^2(z_i e_0 \phi 2k_0 T)}$ (18)

where the bulk volume frac $\bar{\mu}_e = \mu_e^0 + z_e \epsilon_0 \phi + h_n 7 \ln \frac{1}{1-d\epsilon} \sum_{i} n_i = \mu_e^0 + k_n 7 \ln \frac{n_{\text{max}}}{1-2d\epsilon_0 n_i}$

The number density of ion *i* is obtained as,
 $n_i = \frac{n^{\text{deg}} \exp(-z_e \epsilon_0 \phi h_n^0)}{1 + 2\epsilon_0 \sinh(z_e \epsilon_0 \phi h_n^0)}$ (18)

where the bulk volume fractio The number density of ion *i* is obtained as,
 $n_i = \frac{n^2 \exp(-z_i e_0 \phi h_n T)}{1 + 2 \sinh(i \xi_i e_0 \phi/2 h_n T)}$ (18)

where the bulk volume fraction of solvated ions is $v = 2d_i^2 n^3$. The GCS model assumes $v = 0$.

Combining Eq. (2) and E $n_i = \frac{n^2 \exp(-z_i e_0 \phi h k_B T)}{1 + 2 \sinh^2(z_i e_0 \phi/2k_B T)}$ (18)

Where the bulk volume fraction of solvated ions is $n = 2d_i^2 n^b$. The GCS model assumes $n = 0$.

Combining Eq. (2) and Eq. (18), the BPB model is described as,
 $\nabla (\$ the $\pi_i = \frac{1 + 2x\sinh^2(t, e_0 + e_0/2k_0/T)}{1 + 2x\sinh^2(t, e_0 + e_0/2k_0/T)}$ (18)
where the bulk volume fraction of solvated ions is $e = 2d_i^2v^3$. The GCS model assumes $v = 0$.
Combining Γ_0 , (2) and Γ_0 (18), the BPB mode where the bulk volume fraction of solvated ions is $v = 2d_1/v$. The GCS model assumes $v = 0$.

Combining Eq. (2) and Eq. (18), the BPB model is described as,
 $\nabla (\epsilon, \nabla \phi) = \frac{2r^h \epsilon_{c, \text{cosh}} \ln \left(\epsilon_{c, \text{cosh}} \Psi h \right)}{1 + 2 \epsilon \sin$ Combining Eq. (2) and Eq. (18), the BPB model is described as,
 $\nabla (\epsilon, \nabla \phi) = \frac{2\alpha_{\epsilon}^2 \epsilon_0 \sinh(\epsilon_1 \epsilon_0 \phi/\hbar_0 T)}{1 - 2 \cosh^2(\epsilon_1 \epsilon_0 \phi/\hbar_0 T)}$ (19)

In a one dimensional case, the dimensionless form is,
 $\frac{\partial^2 U}{\partial \lambda^2}$

²⁻¹ ⁻³⁻¹ ⁻³⁻ ⁻⁴ ²*-* ⁻³⁻ ² ⁻⁴ ² ⁻⁴ ² ⁻⁴ ² **Figure 6** Typical results of the BPB model, including the spatial distributions of the electric potential and the anion concentration

and assets of electrical potential in (A) and the relationships between (C) the surfa the electric potential and the anion concentration
he surface charge density (D) the differential dou-
the results of the GCS model are shown in the
of this model is provided in the supporting infor-
iccating smaller valu at a series of electrode potential in (A) and (B), and the relationships between (C) the surface charge oble-layer capacitance with the electrode potential. For the purpose of comparison, the results of the black solid li

n. (color on line)

. At larger *v*, the relationship between σ_M and ϕ_M is less steep, indicating smaller value of C_a changes from a camel shape with the minimum at ϕ_{rec} to a bell shape vyshev gives a criti -layer capacitance with the electrode potential. For the purpose of comparison, the results of the GCS model are shown in the ck solutions. The parameters for calculation are listed in Table 1. Matlab script of this model

$$
\bar{\mu}_i = \mu_i^0 + z_i e_0 \phi + k_\text{B} T \ln \frac{d_i^3 n_i}{1 - d_i^3 \sum_i \gamma_i n_i} \tag{22}
$$

where γ_i is the size coefficient,

$$
\gamma_i = \left(\frac{d_i}{d_t}\right)^3\tag{23}
$$

 $,$

$$
\frac{\text{E} \& \frac{\omega}{2}(J. \text{ Electrochem.}) 2022, 28(2), 2108471 \ (11 \text{ of } 30)}{\frac{1 + \frac{v}{2}(\gamma_+ e^{-U} + \gamma_- e^U - \gamma_+ - \gamma_-)}{(24)}}
$$
\nTo obtain Eq. (24), γ_+ and γ_- in the exponent are approximated as 1. Combining Eq. (2), the dimensionless form of the BPB equation in a one-dimensional case is,
\n
$$
\frac{\partial^2 U}{\partial X^2} = \frac{\sinh U}{1 + \frac{v}{2}(\gamma_+ e^{-U} + \gamma_- e^U - \gamma_+ - \gamma_-)} \tag{25}
$$
\nTypical results of the asymmetric BPB model are presented in Figure 7, showing how σ_M and C_d change with

$$
\frac{\partial^2 U}{\partial X^2} = \frac{\sinh U}{1 + \frac{v}{2} (\gamma_+ e^{-U} + \gamma_- e^{U} - \gamma_+ - \gamma_-)}
$$
(25)

The asymmetric BPB model are presented in Figure 7, showing how σ_M and C_d change with
 $\frac{U^2}{1+\frac{p}{2}-(\gamma,e^{-\gamma}+\gamma,e^{\gamma}-\gamma-)}$ (24)

the BPB equation in a one-dimensional case is,
 $\frac{U}{(t^2)} = \frac{\sinh U}{1+\frac{p}{2}(\gamma,e^{-\gamma}+\gamma$ $\frac{\text{d}E}{n} = \frac{n^k e^{i\theta}}{1 + \frac{\nu}{2} (\gamma_i e^{i\theta} + \gamma \cdot e^{i\theta} - \gamma_i - \gamma_i)}$ (24)

To obtain Eq.(24), γ and γ , in the exponent are approximated as 1. Combining Eq.(2), the dimensionless form

of the BPB equation in a one-dim $n_1 = \frac{n^5 e^{2\pi i}}{1 + \frac{p}{2} - (\gamma_e e^{-\gamma} + \gamma_e e^{\gamma} - \gamma_e - \gamma_e)}$ (24)

To obtain Eq.(24), γ, and γ, in the exponent are approximated as 1. Combining Eq.(2), the dimensionless form

To obtain Eq.(24), γ, and γ, in the exponent ar Slectrochem.) 2022, 28(2), 2108471 (11 of 30)

ent are approximated as 1. Combining Eq.(2), the dimensionless form

case is,

(25)

model are presented in Figure 7, showing how σ_M and C_a change with

nts. We set $v =$ $u_1 \equiv \frac{n e^{3x}}{1 + \frac{x}{2}} (\gamma x^{e} + \gamma e^{e} - \gamma, - \gamma)$ (24)

To obtain Eq.(24), γ , and γ in the exponent are approximated as 1. Combining Eq.(2), the dimensionless form

To be EPB equation in a one-dimensional case is,
 $\frac{\$ $n_e = \frac{n_e r^2}{1 + \frac{\mu}{2} (\gamma_e e^{x} + \gamma \cdot e^{x} - \gamma_+ - \gamma_+)}$ (24)

To obtain Eq.(24), γ , and γ_+ in the exponent are approximated as 1. Combining Eq.(2), the dimensionless form

of the BPR equation in a one-dimensional case is $\frac{h}{dt} \mathcal{L}^{\infty}(L \text{ }Electrochem.) 2022, 28(2), 2108471 (11 of 30)$
 $\frac{h}{dt} \frac{v}{2} (\gamma, e^{-t} + \gamma, e^{t} - \gamma, - \gamma)$

To obtain Eq.(24), γ , and γ , in the exponent are approximated as 1. Combining Eq.(2), the dimensionles

of the BP **IEV**

In the EV (*LEhernochem.*) 2022, 28(2), 2108471 (11 of 30)

IT $\frac{1}{2} (\gamma_i e^{i\zeta_i} + \gamma_i e^{i\zeta_i} - \gamma_i - \gamma_i)$

(24)

Obtin Eq.(2), γ_i and γ_i in the exponent are approximated as 1. Combining Eq.(2), the dimensionle

 $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{e^{2\varphi}}{4}$ $\frac{1}{2}$ $\frac{e^{2\var$ $n_x = \frac{n^2e^{7x}}{1 + \frac{\mu}{2}(\gamma_e e^{x} + \gamma_e e^{x} - \gamma_+ - \gamma_-)}$

To obtain Eq.(24), γ_+ and γ_- in the exponent are approximated as 1. Combining Eq.(2), the dimensionless form

of the BPB equation in a one-dimensional case is,
 $n_e = \frac{\alpha_e}{1 + \frac{\beta_e}{2} + \gamma_e e^2 - \gamma_e - \gamma_e}$

To obtain Eq.(24), γ , and γ , in the exponent are approximated as 1. Combining Eq.(2), the dimensionless form

of the BPB equation in a one-dimensional case is,
 $\frac{\partial U}{\partial X^2} = \$ To the HP = $\frac{1}{\sqrt{2}}$ ($r_x = \frac{1}{r_x} = \frac{1}{r^2}$)
To the BPB equation in a one-dimensional case is,
 $\frac{\partial^2 U}{\partial X^2} = \frac{\sinh U}{1 + \frac{\partial^2}{2}(\gamma e^{i\theta} + \gamma e^{i\theta} - \gamma - \gamma)}$ (25)

Typical results of the asymmetric BPB model are prese To obtain Eq.(24), γ , and γ , in the exponent are approximated as 1. Combining Eq.(2), the dimensionless form

of the BPB equation in a one-dimensional case is,
 $\frac{\partial^2 U}{\partial X^2} = \frac{\sinh U}{1 + \frac{v}{2} - (\gamma e^{-U} + \gamma e^U - \gamma, - \gamma)}$ of the BPB equation in a one-dimensional case is,
 $\frac{\partial U}{\partial N^2} = \frac{1}{1 + \frac{b}{2}} (\gamma_e e^{i\omega} + \gamma_e e^i - \gamma_+ - \gamma_+)$

Typical results of the asymmetric BPB model are presented in Figure 7, showing how σ_N and C_α char
 $\frac{\partial V$ $\frac{U}{U^2} = \frac{\sinh U}{1 + \frac{\pi}{2} (\gamma_x e^{-x} + \gamma_z e^v - \gamma_z)}$ (25)
Typical results of the asymmetric BPB model are presented in Figure 7, showing how σ_x and C_a change with
Typical results of the constant size coefficients. We set (25)

In Figure 7, showing how σ_M and C_d change with

and the size coefficient of cations, γ_+ , or that of

veen σ_M and ϕ_M is less steep, indicating smaller

see the concentration of cations dominates in thi 1+ $\frac{1}{2}$ ($y, e^x + y, e^x - y, -y$)

Typical results of the asymmetric BPB model are presented in Figure 7, showing how σ_x and C_a change x
 ϕ_x for the eases of different size coefficients. We set $v = 0.05$, and the

$$
\Omega = U - TS - \int \mathrm{d}V \sum_{i} \bar{\mu}_{i} n_{i} \tag{26}
$$

电化学(*J. Electrochem.*) 2022, 28(2), 2108471 (12 of 30)

S the entropy, $\overline{\mu}_i$ the electrochemical potential of particle *i*, n_i the number density

it.

solvent molecules in the electrolyte solution in general. Ions

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Where *U* is the internal energy, *S* the entropy, $\overline{\mu}_i$ the electrochemical potential of particle *i*, n_i the number density

of particle *i*, the electrochemical potential of particle *i*, n_i the number density
the electrochemical potential of particle *i*, n_i the number density
is in the electrolyte solution in general. Ions, denoted with a sub-
density n the number density
the number density
that a sub-
enoted with a sub- $\exists k \mathcal{L}(J. Electron.)$
 $\exists k \mathcal{L}(J. Electron.)$ 2022, 28(2), 2108471 (12 of 30)

where *U* is the internal energy, *S* the entropy, $\overline{\mu}_i$ the electrochemical potential of particle *i*, n_i the number of

of particle *i*, dV the vol the *I*e $E^{\#}(L \text{ Electrochem.})$ 2022, 28(2), 2108471 (12 of 30)

nere *U* is the internal energy, *S* the entropy, $\overline{\mu}_i$ the electrochemical potential of particle *i*, *n_i* the number density

particle *i*, d*V* the volu **script** $k \neq (L \text{ Electrochem.})$ **2022, 28(2), 2108471 (12 of 30)**
where *U* is the internal energy, *S* the entropy, $\overline{\mu}_i$ the electrochemical potential of particle *i*, *n_i* the number density
of particle *i*, *dV* the vo $\# \{E\}^{\omega}(L \text{ Electrochem.})$ 2022, 28(2), 2108471 (12 of 30)
where *U* is the internal energy, *S* the entropy, $\overline{\mu}_i$ the electrochemical potential of particle *i*, *n_i* the number density
of particle *i*, *dV* the volume $\pm R\mathcal{L}(L)$ Electrochem, 2022, 28(2), 2108471 (12 of 30)

where *U* is the internal energy, *S* the entropy, $\bar{\mu}_i$ the electrochemical potential of particle *i*, *n_i* the number density

of particle *i*, *dV* the $\mathbb{E}(\mathcal{H}, E_{\text{lectroche}})$ 2022, 28(2), 2108471 (12 of 30)
where *U* is the internal energy, *S* the entropy, $\overline{\mu}_i$ the electrochemical potential of particle *i*, *n*, the number density
of particle *i*, *dV* the volume $\#E\#(J. Electron, p)$ 2022, 28(2), 2108471 (12 of 30)
where *U* is the internal energy, *S* the entropy, $\overline{\mu}_i$ the electrochemical potential of particle *i*, *n_i* the num
of particle *i*, *dV* the volume unit.
There are $\frac{16}{2}$ + Electrochemo > 2022, 28(2), 2108471 (12 of 30)

the internal energy, *S* the entropy, $\overline{\mu}$, the electrochemical potential of particle *i*, *n*, the number density
 i, *dV* the volume unit.

re multipl **EVALUATE CONSTRANT (2018671**) (2018671) (201867) (1201867)

Where *U* is the internal energy, *S* the entropy, $\bar{\mu}_i$, the electrochemical potential of particle *i*, *n*, the number density

There are multiple ions and the $R^2(x)$ Electroschene, 2022, 28(2), 2108471 (12 of 30)

where *U* is the internal energy, *S* the entropy, *μ*_{*x*} the electrostencial potential of particle *i*, *n_i* the number density

"There is a modifie ions **EVALUATION ENERT (I.** Electroschem.) 2022, 28(2), 2108471 (12 of 30)

where *U* is the internal energy, *S* the entropy, $\overline{\mu}_t$ the electroshemical potential of particle *i*, *n*, the number density

of particle *i*, The total entropy S is calculated from the lattice-gas model^[48], (29130)

The contropy, S the entropy, μ , the electrochemical potential of particle i , n , the number density

particle i , dV the volume unit.

Th of particle *i*, dV the volume unit.

There are multiple ions and solvent molecules in the electrolyte solution in general. Ions, denoted with a subscript α , have a change number density n_a . There is a population of where $\frac{N}{N}$. The last term accounts for many-body interactions of the particle number of lattice distinguish in the volume in N_{tot} and N_{tot} are the particles are denoted with a subscript s. These charged par

$$
U = \int dV \left(-\frac{1}{2} \epsilon_{s} (\nabla \phi)^{2} + e_{0} \phi \sum (z_{\alpha} n_{\alpha} + z_{\alpha^{*}} n_{\alpha^{*}}) + \sum (n_{\alpha} H_{\alpha} + n_{\alpha^{*}} (H_{\alpha} + E_{\alpha \alpha^{*}})) \right) \tag{27}
$$

field, $-\frac{1}{2}\epsilon_s(\nabla \phi)^2$, and the electrostatic free energy $\frac{1}{2}$ ϵ_s $(\nabla \phi)^2$, and the electrostatic free energies of section to be the volume process α , econous with a septency α . Softwar modelles at both ground and excited state
variables for the volume forces among others. According to field theoretic studies of the coulombic fl or sources with a superstart V . sources are considered with a superstandant and $(z_4z_4 + z_6z_7u_6 + z_1z_8u_7u_8 + z_1z_6u_8u_9 + z_1z_6u_8u_9 + z_1z_6u_8u_9 + z_1z_6u_8u_9 + z_2z_6u_8u_9 + z_2z_6u_8u_9 + z_3z_6u_8u_9 + z_4z_6u_8u_9 + z_6u$ For a note of many $\sum_{k=1}^{n} U_k \left(\frac{N}{N} \right)^{n}$ (29)

The lattice cells are fund without any vacancy, thus N_1 is given by
 U is expressed as,
 $= \int dV \left(-\frac{1}{2} \epsilon_n (\nabla \phi)^2 + e_0 \phi \sum (z_n n_n + z_n n_n) + \sum (n_n H_n + n_n (H_n + E_{n_n})) \right)$ its at som giodal and exerted states, interact

udies of the coulombic fluid^{[51, 52}], the internal
 E_{star}))

ing the self-energy correction of the electric
 $\sigma \Phi \sum z_a n_{\text{ex}}$ and that of the transition-state ions,

 $,$

$$
S = \sum k_B \ln P
$$
\nwhere *P* is the number of ways arranging all the particles in the volume unit dV.

\n(28)

$$
P = \frac{N_{\rm t}!}{\prod N_{\alpha}! N_{\rm s}! \prod N_{\alpha^*}!} \tag{29}
$$

$$
N_{\rm s} = \frac{N_{\rm t}}{\gamma_{\rm s}} - \sum \left(\frac{N_{\alpha} \gamma_{\alpha}}{\gamma_{\rm s}} \right) - \sum \left(\frac{N_{\alpha^{\prime\prime}} \gamma_{\alpha^{\prime\prime}}}{\gamma_{\rm s}} \right) \tag{30}
$$

the last term accounts for many-body interactions other than the electrostatic interactions, with H_a

and energy except the electrostatic contribution, E_{tar} , the activation energy of ion hopping.

tropy *S* is calc ccounts for many-body interactions other than the electrostatic interactions, with *H*_a

cept the electrostatic contribution, *E*_{ac}, the activation energy of ion hopping.

ulated from the lattice-gas model^[48],

y $U = \int dV \left[-\frac{1}{2} - \xi(\sqrt{b}) + \sigma_0 \Phi \right] \Delta (z_i n_i + z_i_n n_{i'} + n_{i'} (H_i + K_{i''}))$ (27)
The first two terms represent the electrostatic interactions, including the self-energy correction of the electric
field, $-\frac{1}{2} - \xi(\sqrt{b})^2$, and t The first two terms represent the electrostatic interactions, including the self-energy correction of the electric

field, $-\frac{1}{2} \epsilon_0 (\nabla \phi)^2$, and the electrostatic free energies of the ions, $e_0 \phi \Sigma z_i \Delta v_i \Delta v_i$. The l field, $-\frac{1}{2} \epsilon_6(\nabla \phi)^2$, and the electrostatic free energies of the ions, $e_6 \phi \sum z_a n_a$ and that of the transition-state ions,
 $e_6 \phi \sum z_a n_a$. The last term accounts for many-body interactions other than the electros For $\frac{N_2}{2}$ extrap, The last term accountance for energies on the standary expression in the causar
orthogology the being and Huang and Huang, there are the activation energy of ion hopping.
The total entropy S is cal eeds $\Sigma_{\alpha,-n,n}$. The last term accounts for many-body interactions other than the electrostatic interactions, with H_n
being the interal arengy except the electrostatic contribution, R_{n_0} , the activation energy of i ing the internal energy except the electrostatic contribution, E_{av} the activation energy of ion hopping.
The total entropy S is calculated from the lattice-gas model^{log},
 $\sum E_{\text{sh}} \ln P$ (28)
 $\sum E_{\text{sh}} \ln P$ (29)
 The total entropy *S* is calculated from the lattice-gas model⁴⁶⁸,

S = $\sum k_n \ln P$

where P is the number of ways arranging all the particles in the volume unit dV,

where $N_n = n_n dV$, $N_1 = n_n dV$, and $N_{n^*} = n_{n^*} dV$ a cells are fully occupied without any vacancy, thus N_i is given by,
 $\left(\frac{N_s \gamma_s}{\gamma_i}\right) - \sum \left(\frac{N_{sc} \gamma_{sc}}{\gamma_s}\right)$ (30)
 $\left(\frac{N_s \gamma_s}{\gamma_s}\right) - \sum \left(\frac{N_{sc} \gamma_{sc}}{\gamma_s}\right)$ (30)
 $\left(\frac{N_s \gamma_{sc}}{\gamma_s}\right)$ (30)
 $\left(\frac{N_s \gamma_{sc}}{\gamma_s}\right)$ (30)
 $\frac{N_c!}{\prod N_c! N_c! \prod N_{ac}!}$ (29)

ere $N_s = n_s \, dV$, $N_c = n_s dV$, and $N_{ac} = n_{ac} dV$ are the particle numbers, and $N_i = n_i dV$ is the total number of lattice

lls in the volume unit, with n_i the number density.

The lattice cell $\prod_{N_{\alpha}} \ln N_{\alpha} \cdot \prod_{N_{\alpha}-1} N_{\alpha} \cdot \prod_{N_{\alpha}} \cdot \prod_{N_{\$ The lattice cells are fully occupied without any vacancy, thus N, is given by,
 $N_s = \frac{N_s}{\gamma_s} - \sum \left(\frac{N_s \gamma_{sc}}{y_s} \right) - \sum \left(\frac{N_{sc} \gamma_{sc}}{y_s} \right)$ (30)

Note that there are several methods to treat size asymmetry in the latt $\sum (\frac{N_2 n}{\gamma} - \sum |\frac{N_2 n}{\gamma} - \gamma|$ (30)

there are several methods to treat size asymmetry in the lattice-gas model, as recently compared by

Huang¹⁸⁶. What we have used in Eqs. (29) and (30) is Huang's treatment⁸³. Th

$$
S = -\int dV k_{\rm B} \left(\sum n_{\alpha} \ln \frac{n_{\alpha}}{n_{\rm t}} + n_{\rm s} \ln \frac{n_{\rm s}}{n_{\rm t}} + \sum n_{\alpha^{\mu}} \ln \frac{n_{\alpha^{\mu}}}{n_{\rm t}} + n_{\rm t} - \sum n_{\alpha} - n_{\rm s} - \sum n_{\alpha^{\mu}} \right) \tag{31}
$$

$$
\Omega = \int f dV \tag{32}
$$

Using the starting formula and using the continuous limit (transversing the summation to a volume integration),
\nwe reformulate Eq. (28) as,
\n
$$
S = -\int dV k_B \left(\sum n_a \ln \frac{n_a}{n_t} + n_s \ln \frac{n_s}{n_t} + \sum n_{\alpha} \ln \frac{n_{\alpha}^2}{n_t} + n_t - \sum n_{\alpha} - n_s - \sum n_{\alpha} \right)
$$
\n(31)
\nCombining Eqs. (26), (27), and (31), we rewrite the grand potential as a volume integration of a volumetric
\ngrand potential,
\n
$$
\Omega = \int f dV
$$
\n(32)
\nwith the volumetric grand potential f given by,
\n
$$
f = -\frac{1}{2} \epsilon_s (\nabla \phi)^2 + e_{\phi} \phi \sum (z_a n_{\alpha} + z_{\alpha} n_{\alpha}^2) + \sum (n_a H_a + n_{\alpha} (H_a + E_{aa}^2)) +
$$
\n
$$
\frac{1}{\beta} \left(\sum n_a \ln \frac{n_a}{n_t} + n_s \ln \frac{n_s}{n_t} + \sum n_{\alpha} \ln \frac{n_{\alpha}^2}{n_t} + n_t - \sum n_{\alpha} - n_s - \sum n_{\alpha} \right) - \left(\sum \overline{\mu}_{\alpha} n_{\alpha} + \overline{\mu}_{\alpha} n_s + \sum \overline{\mu}_{\alpha} n_{\alpha} \right)
$$
\n(33)

$$
\text{H}(k \neq (J. Electrochem.) 2022, 28(2), 2108471 (13 of 30))}
$$
\nUsing the Euler-Lagrange equation,
\n
$$
\frac{\partial f}{\partial X} - \nabla \left(\frac{\partial f}{\partial (\nabla X)} \right) = 0
$$
\n
$$
\text{in terms of } X = \phi \text{, we obtain the Poisson equation,}
$$
\n
$$
\frac{\partial}{\partial \phi} \left(\frac{\partial f}{\partial \phi} \right) = \sum_{X \in \mathcal{X}} \phi(X) \phi(X) \phi(X) \tag{35}
$$

$$
\text{E} \{E \neq (J. \text{ Electrochem.}) 2022, 28(2), 2108471 (13 of 30)}
$$
\nUsing the Euler-Lagrange equation,

\n
$$
\frac{\partial f}{\partial X} - \nabla \left(\frac{\partial f}{\partial (\nabla X)} \right) = 0
$$
\n(34)

\nin terms of $X = \phi$, we obtain the Poisson equation,

\n
$$
\frac{\partial}{\partial x} \left(\epsilon_s \frac{\partial \phi}{\partial x} \right) = -e_0 \sum (z_a n_\alpha + z_{\alpha'} n_{\alpha'})
$$
\n(35)

\nWhen applying the Euler-Lagrange equation in terms of $X = n_\alpha$, we must take notice of the relation that $n_s = n/\gamma_s - \sum n_s \gamma / \gamma_s - \sum n_{\alpha'} \gamma_s / \gamma_s$ is also a function of n_α . Therefore, adding an ion α will simultaneously reduce γ / γ_s .

 $\frac{\text{ft}(E^{\text{int}})(L \text{ Electrow-}hem, 2022, 28(2), 2108471 (13 of 30))}{\text{Euler-Lagrange equation,}}$

Euler-Lagrange equation,
 $\left(\frac{\partial f}{\partial(\overline{Y}X)}\right) = 0$ (34)
 $fX = \phi$, we obtain the Poisson equation,
 $\frac{b}{\phi} = -e_0 \sum (z_d\pi_d + z_{\alpha}r_{\alpha}')$ (35)

applyin $\frac{d_1}{dt} \mathcal{L}^{\#}(L \text{ Electrochem.}) 2022, 28(2), 2108471 (13 of 30)$

g the Euler-Lagrange equation,
 $-\nabla \left(\frac{\partial f}{\partial (YX)} \right) = 0$ (34)

rms of $X = \phi$, we obtain the Poisson equation,
 $\left[\epsilon, \frac{\partial \phi}{\partial x} \right] = -\epsilon_0 \sum (z_n n_n + z_n n_n)$ (35)
 $\frac{dE}{dt} \frac{dE}{dt} \frac{dE}{dt}$ (*Klectrochem.*) 2022, 28(2), 2108471 (13 of 30)
 $\frac{c}{\epsilon} - \nabla \left(\frac{\partial f}{\partial(\nabla X)} \right) = 0$ (34)

terms of *X* = *φ*, we obtain the Poisson equation,
 $\left[\epsilon_n \frac{\partial \phi}{\partial x} \right] = -e_0 \sum (z_a n_a + z_a n_a)$ (35 $n_v/\gamma_s - \sum n_{\alpha} \gamma_d/\gamma_s - \sum n_{\alpha^*} \gamma_{\alpha^*}/\gamma_s$ is also a function of n_{α} . There is a flexon equation,

interaction of n_α. Therefore, adding an ion α will simultaneously reduce γ_α/γ_s (35)

Lagrange equation in terms of $X = n_{\infty}$, we must take notice of the relation that $n_s =$

is also a funct the Euler-Lagrange equation,
 $\frac{\partial f}{\partial X} - \nabla \left(\frac{\partial f}{\partial (Y X)} \right) = 0$ (34)
 $\frac{\partial f}{\partial X} - \nabla \left(\frac{\partial f}{\partial (Y X)} \right) = 0$ (34)

in terms of $X = \phi$, we obtain the Poisson equation,
 $\frac{\partial}{\partial x} \left(\epsilon, \frac{\partial \phi}{\partial x} \right) = -e_0 \sum (x_n + z_\omega n_\$ $+$ $\frac{1}{2}$ + $\frac{1}{2}$ + betweekem.) 2022, 28(2), 2108471 (13 of 30)

(34)

uation,

(35)

usion,

(35)

tion in terms of $X = n_{\infty}$, we must take notice of the relation that $n_{\infty} =$

to,
 n_{∞} . Therefore, adding an ion α will simultaneo **finally** the Euler-Lagrange equation,

Using the Euler-Lagrange equation,
 $\frac{\partial f}{\partial x} - \nabla \left(\frac{\partial f}{\partial (\nabla x)} \right) = 0$ (34)

in terms of $X = \phi$, we obtain the Poisson equation,
 $\frac{\partial}{\partial x} \left(\frac{e}{\omega} \frac{\partial f}{\partial x} \right) = -e_0 \sum (z_a u$ **EVALUATION 19.** $\frac{d\mathbf{f}(\mathcal{V})}{dt}$ (13 of 30)

Using the Euler-Lagrange equation,
 $\frac{\partial f}{\partial x} - \nabla \left(\frac{\partial f}{\partial (\nabla X)} \right) = 0$ (34)

in terms of $X = \phi$, we obtain the Poisson equation,
 $\frac{\partial}{\partial x} \left(\epsilon \frac{\partial \phi}{\partial x} \right) = -\epsilon_$ Using the Euler-Lagrange equation,
 $\frac{\partial}{\partial x} - \nabla \left[\frac{\partial d_0}{\partial (\nabla X)} \right] = 0$ (34)
 $\frac{\partial}{\partial x} - \nabla \left[\frac{\partial d_0}{\partial (\nabla X)} \right] = 0$ (35)

in terms of $X = \phi$, we obtain the Poisson equation,
 $\frac{\partial}{\partial x} \left(\epsilon, \frac{\partial \phi}{\partial x} \right) = -\epsilon_0$ $\frac{\partial}{\partial x}$ \ θ (v x) |

in terms of X = φ, we obtain the Poisson equation,
 $\frac{\partial}{\partial x} \left[\epsilon, \frac{\partial \phi}{\partial x} \right] = -e_0 \sum (z_a u_a + z_a r u_a)$

When applying the Euler-Lagrange equation in terms of X = n_a, we must take notice
 n in terms of $X = \phi$, we obtain the Poisson equation,
 $\frac{\partial}{\partial x} \left(\epsilon, \frac{\partial}{\partial x} \right) = -\epsilon_0 \sum (z_i n_x + z_n n_x)$

When applying the Euler-Lagrange equation in terms of $X = n_x$, we must take notice of the relation that $n_x = n_x \gamma_x - \gamma_x$. $\frac{\partial}{\partial x} \left(\varepsilon_2 \frac{\partial \phi}{\partial x} \right) = -\varepsilon_0 \sum (z_i n_{\rm s} + z_{\rm s} n_{\rm s})$ (35)

When applying the Euler-Lagrange equation in terms of $X = n_{\rm a}$, we must take notice of the relation that $n_{\rm s} = n/\gamma_s - \sum n_{\rm s} \gamma_r \rightarrow \sum n_{\rm s} \gamma_r \rightarrow \gamma$ When applying the Euler-Lagrange equation in terms of $X = n_{\alpha}$, we must take notice of the relation that $n_{\alpha} = \mu_{\alpha} = \mu_{$

$$
n_{\ell}\gamma_{s} - 2n_{\alpha}\gamma_{s}\gamma_{s} - 2n_{\alpha}\gamma_{\alpha}\gamma_{s}
$$
 is also a function of n_{α} . Therefore, a
solvent molecules. The consideration leads to,
 $z_{\alpha\beta}\phi + H_{\alpha} + \frac{1}{\beta} \left(\ln \frac{n_{\alpha}}{n_{\tau}} - \frac{\gamma_{\alpha}}{\gamma_{s}} \ln \frac{n_{\alpha}}{n_{\tau}} \right) - \bar{\mu}_{\alpha} + \frac{\gamma_{\alpha}}{\gamma_{s}} \bar{\mu}_{s} = 0$ (36)
from which we define the electrochemical potential of the ion-solvent pair,
 $\bar{\mu}_{\alpha\alpha} = \bar{\mu}_{\alpha} - \frac{\gamma_{\alpha}}{\gamma_{s}} \bar{\mu}_{s}$ (37)
with the electrochemical potential of solvent molecules expressed as,
 $\bar{\mu}_{\alpha} = \frac{1}{\beta} \ln \frac{n_{\alpha}}{n_{\tau}}$ (38)
and the electrochemical potential of ions α as,
 $\bar{\mu}_{\alpha} = H_{\alpha} + z_{\alpha}e_{0}\phi + \frac{1}{\beta} \ln \frac{n_{\alpha}}{n_{\tau}}$ (39)
When the fictitious lattice cells are occupied exclusively by ions α , namely, $n_{\tau} = n_{\alpha}$, the chemical potential turns
to the standard chemical potential of ions α , denoted as μ_{α}^{0} ,
 $\mu_{\alpha}^{0} = H_{\alpha}$ (40)
Applying the Euler-Lagrange equation in terms of $X = n_{\alpha} \tau$, we obtain the standard chemical potential of
transition-state ions α^{π} ,
 $\mu_{\alpha}e^{\alpha} = H_{\alpha} + E_{\alpha\alpha} \tau$ (41)
 Δ Although the transition-state ions are explicitly included in the grand-canonical potential, we will make the
approximate that $n_{\alpha} \ll n_{\alpha}$ in the following.
According to the Fick's second law, the continuity equation for particle α in the i^{th} cubic cell is written as,
(42)

$$
\bar{\mu}_{\alpha\text{-s}} = \bar{\mu}_{\alpha} - \frac{\gamma_{\alpha}}{\gamma_{s}} \bar{\mu}_{\text{s}}
$$
(37)

from which we define the electrochemical potential of the ion-solvent pair,
\n
$$
\bar{\mu}_{\alpha=}\bar{\mu}_{\alpha} - \frac{\gamma_{\alpha}}{\gamma_{\alpha}} \bar{\mu}_{\alpha}
$$
\nwith the electrochemical potential of solvent molecules expressed as,
\n
$$
\bar{\mu}_{\alpha} = \frac{1}{\beta} \ln \frac{n_{\alpha}}{n_{\alpha}}
$$
\n(38)
\nand the electrochemical potential of ions α as,
\n
$$
\bar{\mu}_{\alpha} = H_{\alpha} + z_{\alpha}e_{0}\phi + \frac{1}{\beta} \ln \frac{n_{\alpha}}{n_{\alpha}}
$$
\n(39)
\nWhen the fictitious lattice cells are occupied exclusively by ions α , namely, $n_{\alpha} = n_{\alpha}$, the chemical potential turns
\nto the standard chemical potential of ions α , denoted as μ_{α}^{0} ,
\n
$$
\mu_{\alpha}^{0} = H_{\alpha}
$$
\n(40)
\nApplying the Euler-Lagrange equation in terms of $X = n_{\alpha^{*}}$, we obtain the standard chemical potential of
\ntransition-state ions α^{*} ,
\n
$$
\mu_{\alpha}^{0} = H_{\alpha} + E_{\alpha\alpha^{*}}
$$
\n(41)
\nAlthough the transition-state ions are explicitly included in the grand-canonical potential, we will make the
\napproximate that $n_{\alpha} \ll n_{\alpha}$ in the following.
\nAccording to the Fick's second law, the continuity equation for particle α in the t^{th} cubic cell is written as,
\n
$$
\frac{\partial n_{\alpha}^{i}}{\partial t} = -\frac{\partial J_{\alpha}^{i}}{\partial x}
$$
\n(42)
\nwhere J_{α}^{i} is the flow flux of particle α cross the i^{th} cubic cell, the interface between the i^{th} cubic cell and the $(i+1)^{\text{th}}$

$$
\bar{\mu}_{\alpha} = H_{\alpha} + z_{\alpha}e_0\phi + \frac{1}{\beta}\ln\frac{n_{\alpha}}{n_{\text{t}}} \tag{39}
$$

0 $,$

$$
\boldsymbol{\mu_{\alpha}}^0 = \boldsymbol{H_{\alpha}}
$$

(40)

$$
\mu_{\alpha^*}{}^0 = H_\alpha + E_{\alpha \alpha^*} \tag{41}
$$

 $\pi_x \alpha_5 \phi + H_x + \frac{1}{\beta} \left(\ln \frac{n_x}{n_x} - \frac{\gamma_x}{\gamma_x} \ln \frac{n_x}{n_x} \right) - \overline{\mu_x} + \frac{2\omega_x}{\gamma_x} \overline{\mu_x} = 0$ (36)

from which we define the cletredenemical potential of the ion-solvent pair,
 $\mu_{\omega_0} = \mu_0 - \frac{2\omega_x}{\gamma_x} \mu_S$ (37)

with the According to the form of the content of the form of the second as $\frac{1}{\beta} \bar{\mu}_n = \frac{\gamma_L}{\gamma_L} \bar{\mu}_s$ (37)
 $\frac{1}{\beta} \ln \frac{n_i}{n_i}$ (38)
 $= \frac{1}{\beta} \ln \frac{n_i}{n_i}$ (38)
 $= H_n + z_n e_0 \phi + \frac{1}{\beta} \ln \frac{n_x}{n_i}$ (39)

the electrochemical p (37)

(38)

(38)

the chemical potential turns

(40)

mdard chemical potential of

(41)

potential, we will make the

th cubic cell is written as,

(42)

ne *i*th cubic cell and the $(i+1)^{th}$

$$
\frac{\partial n_{\alpha}^{i}}{\partial t} = -\frac{\partial J_{\alpha}^{i}}{\partial x} \tag{42}
$$

where J_{α}^{i} is the flow flux of particle α cross the i^{th} cub

$$
\bar{\mu}_s = \frac{1}{\beta} \ln \frac{n_s}{n_t}
$$
\n(38)
\nand the electrochemical potential of ions α as,
\n
$$
\bar{\mu}_\alpha = H_\alpha + z_\alpha e_0 \phi + \frac{1}{\beta} \ln \frac{n_\alpha}{n_t}
$$
\n(39)
\nWhen the fictitious lattice cells are occupied exclusively by ions α, namely, n_t = n_\omega the chemical potential turns
\nto the standard chemical potential of ions α, denoted as μ_\alpha^\theta,\n
$$
\mu_\alpha^0 = H_\alpha
$$
\n(40)
\nApplying the Euler-Lagrange equation in terms of $X = n_\alpha$, we obtain the standard chemical potential of
\ntransitions-state ions α^π,
\n(41)
\nAlthough the transition-state ions are explicitly included in the grand-canonical potential, we will make the
\napproximate that n_α < m_\alpha in the following.
\nAccording to the Fick's second law, the continuity equation for particle α in the ith cubic cell is written as,
\n
$$
\frac{\partial n_\alpha^i}{\partial t} = -\frac{\partial I_\alpha^i}{\partial x}
$$
\n(42)
\nwhere
$$
J_\alpha^i
$$
 is the flow flux of particle α cross the ith cubic cell, the interface between the ith cubic cell and the (i+1)th
\ncubic cell,
\n
$$
J_\alpha^i = J_\alpha^{i-i+1} - J_\alpha^{i+1-i} = \frac{1}{d_i^2} \left(k_\alpha^{i-i+1} \frac{n_\alpha^{i+1}}{n_i} - k_\alpha^{i+1-i} \frac{n_\alpha^{i+1}}{n_i} - k_\alpha^{i+1-i} \frac{n_\alpha^{i+1}}{n_i} \frac{n_\alpha^{i+1}}{n_i} \right)
$$
\n(43)
\nEq.(43) means that the ion transport process is pictured as an ion-solvent exchange reaction, which has been

 $\overline{\mu}_s = \frac{1}{\beta} \ln \frac{n_s}{n_i}$
and the electrochemical potential of ions α as,
 $\overline{\mu}_\alpha = H_\alpha + z_\alpha e_0 \phi + \frac{1}{\beta} \ln \frac{n_\alpha}{n_i}$
When the fictitious lattice cells are occupied exclusively by ions α , namely, $n_i = n_\omega$
to the Lagrange equation in terms of $X = n_{\alpha^*}$, we obtain the standard chemical potential of
 (40)

state ions are explicitly included in the grand-canonical potential, we will make the
 μ in the following.
 \int 's second $= H_a + z_a e_0 \phi + \frac{1}{\beta} \ln \frac{n_a}{n_a}$ (39)

then the fictitious lattice cells are occupied exclusively by ions α , annely, $n_i = n_a$ the elemnical potential turns

the standard chemical potential of ions α , denoted as $\mu_a^$ When the fictitious lattice cells are occupied exclusively by ions α , namely, $n_x = n_{\omega}$ the chemical potential turns
to the standard chemical potential of ions α , denoted as μ_n^{β} , (40)
 $\mu_n^{\beta} = H_n$ (40)
 μ_n $i^{\rightarrow i+1}$ and $k_{\alpha}^{i+1\rightarrow i}$ represtructure is the formulation state in the standard elementation of ions α , denoted as μ_n^{β} , $\mu_n^{\beta} = H_{\alpha}$
 $\mu_n^{\beta} = H_{\alpha}$

Applying the Euler-Lagrange equation in terms of $X = n_{\alpha^{-1}}$, we obtain the standard eh (40)
 \cdot , we obtain the standard chemical potential of

the grand-canonical potential, we will make the

for particle α in the *i*th cubic cell is written as,

(42)

interface between the *i*th cubic cell and the (40)
 $u_n^0 = H_n$

Applying the Euler-Lagrange equation in terms of $X = n_n$, we obtain the standard chemical potential of

transition-state ions α^n ,
 $u_n^0 = H_0 + E_{n_0\alpha}$
 $u_n^0 = H_0 + E_{n_0\alpha}$
 $u_n^0 = \frac{3J_n^2}{6\alpha}$
 $u_n^0 =$ $u_n = u_n$
 $u_n = \frac{1}{2} \left(k_n e^{-\alpha} \right) \frac{1}{n} = k_n e^{-\alpha}$
 $\mu_n = \frac{1}{2} \left(\mu_n e^{-\alpha} \right) \frac{1}{n} = k_n e^{-\alpha}$
 $\mu_n = \frac{1}{2} \left(\mu_n e^{-\alpha} \right) \frac{1}{n} = k_n e^{-\alpha}$

Although the thransition-state ions are explicitly included in the grand-canonical and the Gibbs free energy change, we write $k_{\alpha}^{i\rightarrow+1}$ as, I flow flux of particle α cross the *i*ⁿ cubic cell, the interface between the *i*ⁿ cubic cell and the (*i*+1

ⁱ⁺¹ = $\frac{1}{d_x^2}$ [$k_x^{i\to i+1} \frac{n_a^i}{n_a}$ = n_x^{i+1} = $k_x^{i+1-i} \frac{n_a^{i+1}}{n_a}$ = n_x^{i+1} = n_x^{i+1 (42)

the i^{th} cubic cell, the interface between the i^{th} cubic cell and the $(i+1)^{\text{th}}$
 $k_x^{n-1-i} \frac{n_x^{i+1}}{n_t} \frac{n_x^{i}}{n_t}$ (43)

cess is pictured as an ion-solvent exchange reaction, which has been

solid and ^{1→} = $\frac{1}{d_t^2} \left(k_a^{(-4)} \frac{n_a!}{n_t} - \frac{n_b^{(+1)}}{n_t} - k_a^{(+1)} \frac{n_a^{(+1)}}{n_t} - \frac{n_b^{(+1)}}{n_t} \right)$ (43

ns that the ion transport process is pictured as an ion-solvent exchange reaction, which has been

r to describe ion transport in ^{*i*:1-*i*} $\frac{n_a^{i+1}}{n_a} \frac{n_a^{i}}{n_b}$ (43)

ess is pictured as an ion-solvent exchange reaction, which has been

solid and concentrated electrolytes^{[98,54}], where $k_a^{(-4)}$ and $k_a^{(n)-4}$ repre-

hopping from the i^{th}

$$
k_{\alpha}^{\ i\rightarrow i\pm 1} = k_{\alpha}^{\ 0} \exp\left(-\frac{\beta}{2}(\overline{\mu}_{\alpha\rightarrow s}^{\ i\pm 1} - \overline{\mu}_{\alpha\rightarrow s}^{\)}\right) = k_{\alpha}^{\ 0} \exp\left(-\frac{\beta}{2} \nabla \overline{\mu}_{\alpha\rightarrow s} d_{\tau}\right)
$$
(44)

and $k_{\alpha}^{\ i+1\to i}$ as,

$$
k_{\alpha}^{\ i+1-i} = k_{\alpha}^{\ 0} \exp\left(-\frac{\beta}{2} \left(\overline{\mu}_{\alpha-s}^{\ i} - \overline{\mu}_{\alpha-s}^{\ i+1}\right)\right) = k_{\alpha}^{\ 0} \exp\left(\frac{\beta}{2} \nabla \overline{\mu}_{\alpha-s} d_{t}\right)
$$
\n(45)

where the standard rate constant k_{α}^{0} is expressed as,

$$
\text{where the standard rate constant } k_{\alpha}^0 \text{ is expressed as,}
$$
\n
$$
k_{\alpha}^0 = \frac{1}{2\tau_{\alpha 0}} \exp(-\beta(\mu_{\alpha^{\nu}}^0 - \mu_{\alpha}^0)) = \frac{1}{2\tau_{\alpha 0}} \exp(-\beta E_{\alpha \alpha^{\nu}})
$$
\n
$$
\text{with } \tau_{\alpha 0} \text{ being the time constant of the hopping process. The 1/2 here indicates that ions at the transition state are equally likely to go forward to the new state and backward to the original state.}\n\text{Substituting Eqs. (44), (45) and (46) into (43), we rewrite the flux as,}
$$
\n
$$
J_{\alpha} = -\frac{2D_{\alpha}}{d_{\alpha}^{4}} \sinh\left(\frac{\beta}{2} \nabla \bar{\mu}_{\alpha\beta} d_{\alpha}\right) \frac{n_{\alpha}}{n_{\alpha}} \frac{n_{\alpha}}{n_{\alpha}} \tag{47}
$$

$$
\frac{d_2(E_+^{2\alpha}(J. Electrochem.) 2022, 28(2), 2108471 (14 of 30))}{\sqrt{2\pi a}} \exp(-\beta(\mu_{\alpha_0}^0 - \mu_{\alpha_0}^0)) = \frac{1}{2\pi a_0} \exp(-\beta E_{\alpha_0}^0)
$$
\nwith τ_{α_0} being the time constant of the hopping process. The 1/2 here indicates that ions at the transition state are equally likely to go forward to the new state and backward to the original state. Substituting Eqs. (44), (45) and (46) into (43), we rewrite the flux as,
\n
$$
J_{\alpha} = -\frac{2D_{\alpha_0}}{d_1^4} \sinh\left(\frac{\beta}{2} \nabla \bar{\mu}_{\alpha_0} d_1\right) \frac{n_{\alpha_0} n_{\alpha_0}}{n_1 n_1}
$$
\nwhere D_a is the diffusion coefficient,
\n
$$
D_{\alpha} = \frac{d_1^2}{2\pi a_0} \exp(-\beta E_{\alpha_0} \nu)
$$
\n
$$
D_{\alpha} = \frac{d_1^2}{2\pi a_0} \exp(-\beta E_{\alpha_0} \nu)
$$
\n
$$
D_{\alpha} = -D_{\alpha} \beta \frac{n_{\alpha} n_{\alpha}}{n_{\alpha}} \nabla \bar{\mu}_{\alpha_{\alpha}} \n\tag{48}
$$
\nIn the near-equilibrium regime, $\sinh(\beta d_1 \nabla \bar{\mu}_{\alpha_0} / 2) \approx \beta d_1 \nabla \bar{\mu}_{\alpha_{\alpha}} / 2$, Eq. (47) can be approximated to,
\n
$$
J_{\alpha} = -D_{\alpha} \beta \frac{n_{\alpha} n_{\alpha}}{n_{\alpha}} \nabla \bar{\mu}_{\alpha_{\alpha}} \n\tag{49}
$$
\nwhere $\nabla \bar{\mu}_{\alpha_{\alpha}}$ is expanded as,
\n
$$
\nabla \bar{\mu}_{\alpha_{\alpha}} = \frac{1}{\beta n_{\alpha}} \frac{\partial n_{\alpha}}{\partial x} + \frac{1}{\beta n_{\alpha}} \sum_{\gamma} \sum_{\alpha} \sum_{\alpha} \frac{\partial n_{\alpha}}{\partial x} + z_{\alpha} \sigma_{\alpha} \frac{\partial \phi}{\partial x}
$$
\n
$$
D_{\alpha} = -
$$

$$
D_{\alpha} = \frac{d_{\rm t}^2}{2\tau_{\alpha,0}} \exp(-\beta E_{a\alpha^*}) \tag{48}
$$

$$
J_{\alpha} = -D_{\alpha}\beta \frac{n_{\alpha}n_{\rm s}}{n_{\rm t}} \nabla \bar{\mu}_{\alpha - \rm s} \tag{49}
$$

$$
\nabla \overline{\mu}_{\alpha s} = \frac{1}{\beta n_{\alpha}} \frac{\partial n_{\alpha}}{\partial x} + \frac{1}{\beta n_{s}} \frac{\gamma_{\alpha}}{\gamma_{s}} \sum_{i \neq s} \frac{\gamma_{i}}{\gamma_{s}} \frac{\partial n_{i}}{\partial x} + z_{\alpha} e_{0} \frac{\partial \phi}{\partial x}
$$
(50)

$$
\frac{\partial n_{\alpha}}{\partial t} = \frac{\partial}{\partial x} \left(D_{\alpha} \frac{n_{\rm s}}{n_{\rm t}} \frac{\partial n_{\alpha}}{\partial x} + D_{\alpha} \frac{n_{\alpha}}{n_{\rm t}} \frac{\gamma_{\alpha}}{\gamma_{\rm s}} \sum_{i \neq s} \frac{\gamma_{i}}{\gamma_{\rm s}} \frac{\partial n_{i}}{\partial x} + D_{\alpha} \beta \frac{n_{\alpha} n_{\rm s}}{n_{\rm t}} z_{\alpha} e_{0} \frac{\partial \phi}{\partial x} \right) \tag{51}
$$

Substituting Eqs. (4), (4) and (50) into the water and continue the continue of the secondary of \vec{B} , \vec{B} and $\left[\frac{\beta}{2} - \vec{V}_{\mu\nu}d\mu\right] \frac{n_{\nu}}{n_{\nu}} \frac{n_{\nu}}{n_{\nu}}$ (47)
 $= -\frac{2D_{\nu}}{a_{\nu}} \sinh\left[\frac{\beta}{2} - \vec{V}_{\mu\nu}d$ *f* $L = -2D_a$ sink $\left[\frac{\beta}{2} - \nabla \overline{\mu}_a \right]_0^L + \left[\frac{n}{n_1} \frac{n_2}{n_1} \right]_0^L$ (47)

where $D_a = \frac{d^2}{2\tau_{\text{tot}}} \exp(-\beta E_{\text{tot}})$ $\left[\frac{n_2}{n_1} \frac{n_2}{n_1} \right]_0^L$ (48)
 $D_a = \frac{d^2}{2\tau_{\text{tot}}} \exp(-\beta E_{\text{tot}})$ (48)

In the near-equili

the diffusion coefficient,
 $\exp(-\beta E_{cor})$ (48)

equilibrium regime, $\sinh(\beta d, \nabla \bar{\mu}_{cor}/2) \approx \beta d, \nabla \bar{\mu}_{cor}/2$, Eq. (47) can be approximated to,
 $a_n^{n_1} \nabla \bar{\mu}_{\mu_{eq}}$ (49)
 $\frac{\partial n_n}{\partial t} + \frac{\gamma}{\beta \mu_{eq}} \times \frac{\gamma}{\gamma} \sum_{i=1}^n \frac{\partial n$ $f_n = -\frac{\mathcal{L}I_{\text{ex}}}{dt} \sinh \left[\frac{P}{2} - \nabla \overline{\mu}_{\text{ex}} dt\right] \left[\frac{n}{n_1} \frac{n_2}{n_1} \frac{n_3}{n_1} \right]$

where D_n is the diffusion coefficient,
 $D_n = \frac{d_n^2}{n_1} \exp(-\beta E_{\text{ex}})$ (48)

In the near-equilibrium regime, $\sinh(\beta d, \nabla \overline{\mu}_{\$ Let D_a is the diffusion coefficient,
 $=\frac{d_s^2}{2\pi\omega_0}\exp(-\beta E_{\alpha\alpha'})$ (48)
 $2\pi\omega_0$ the near-equilibrium regime, $\sinh(\beta d_x \nabla \mu_{\alpha}/2) \approx \beta d_x \nabla \mu_{\alpha}/2$, Eq. (47) can be approximated to,
 $L_{\alpha\alpha} = -D_a\beta \frac{n_a n_a}{n_a} \nabla \mu_{\$ differential equations. The boundary conditions. The boundary conditions are the boundary conditions are a commonly divided into the boundary conditions are a commonly divided into the boundary conditions are commonly div $D_n = \frac{1}{2\tau_{orb}} \exp(-\beta E_{cor})$

(48)

In the near-equilibrium regime, $\sinh(\beta d$, $\nabla \mu_{av}/2) = \beta d$, $\nabla \mu_{av}/2$, Eq. (47) can be approximated to,
 $\nabla \mu_{av} = \frac{1}{\beta \mu_{av}} \frac{\hbar_{av} \mu_{av}}{\hbar_{av}} = \frac{1}{\beta \mu_{av}} \frac{\hbar_{av}}{\hbar_{av}} + \sum_{v} \frac{\gamma_{v$ mated to,

(49)

(50)

tute the continuum model

e grand potential being a

P equation, a set of partial

D P equation, a set of partial

D P P at x = x₀. Robin

example, $y = y_0$ at $x = x_0$.

Robin

S, for example, $y - \$ $f_n = -H_n\beta - \frac{n}{n_1} \partial_{n_2} + \frac{1}{n_2} \partial_{n_3} + \frac{1}{n_3} \partial_{n_4} + \frac{1}{2} \partial_{n_5} \frac{\partial_{n_6}}{\partial x} + \frac{1}{2} \partial_{n_6} \frac{\partial_{n_7}}{\partial x} + \frac{1}{2} \partial_{n_7} \frac{\partial_{n_8}}{\partial x} + \frac{1}{2} \partial_{n_8} \frac{\partial_{n_9}}{\partial x}$ (50)

Combining Eqs. (42), (49) and (50), we obt boundary conditions are a combination of Dirichlet and Neumann boundary conditions, for example, $y - \frac{\partial y}{\partial y} = 0$ (50)

(51)

a model

being a

f partial

ann and

t $x = x_0$.

Robin
 $\frac{\partial y}{\partial x} = 0$

s are,

(52) $\nabla \overrightarrow{\mu}_{\text{max}} = \frac{1}{\beta h_{\text{in}}} \frac{\partial n_{\text{in}}}{\partial h} + \frac{1}{\beta h_{\text{in}}} \frac{\gamma_{\text{v}}}{\gamma_{\text{v}}} \frac{\gamma_{\text{v}}}{\gamma_{\text{v}}} \frac{\partial n_{\text{v}}}{\partial h} + z_{\beta h_{\text{in}}} \frac{\partial \phi}{\partial h}$ (50)

Combining Eqs. (42), (49) and (50), we obtain a modified Nemst-Planck equat $\frac{\partial n_a}{\partial t} = \frac{\partial}{\partial x} \left(D_s \frac{n_s}{n_i} \frac{\partial n_a}{\partial x} + D_s \frac{n_a}{n_i} \frac{\gamma_a}{\gamma_s} \frac{\sum_i \beta_i}{\gamma_s} \frac{\partial n_i}{\partial x} + D_s \beta \frac{n_a n_s}{n_i} z_x e_0 \frac{\partial \phi}{\partial x} \right)$

The modified Poisson-Nernst-Planck (PNP) equations in Eq. (35) and Eq. (51) cons

for multico The modified Poisson-Nemsth-Planck (PNP) equations in Eq. (35) and Eq. (51) constitute the continuum model
for multicomponent mass transport in electrolyte solution, which is derived from the grand potential being a
funct For multiomponent mass transport in electrolyte solation, which is derived from the grand potential being a
functional of the electric potential and the particle mumber densities.
The boundary conditions and the initial c for manucular
non-intervalsion in testical and the particle number densities.
The boundary conditions and the initial conditions are necessary for solving the PNP equation, a set of partial
differential equations. The bou contained a text of particle mumber of the same as Eq. (8). Eq. (52) is a Neumann boundary conditions the registrode side, which is the same as Eq. (8). Eq. (52) is a Neumann boundary conditions specify the variable value The boundary conductions and the final columbis are necessary for solving the Five
differential equations. The boundary conditions are commonly divided into three types,
Robin. Dirichlet boundary conditions specify the va ieremian equations. The boundary conditions specify the variable value on the boundary, for example, $y = y_0$ at $x = x_0$.

Unim, Dirichlet boundary conditions specify the variable value on the boundary, for example, $y = y_0$ Enterioris: The boundary conditions, the courter optical boundary conditions are continuous and controls, permann and the Richard Boundary conditions specify the derivative of the variable, for example, $\frac{\partial y}{\partial x} = \alpha$ at

$$
J_{\alpha} = m_{\alpha} \frac{j}{me_0} \tag{52}
$$

$$
\phi(0, t) = \phi_{\rm M} - \phi_{\rm px} + \frac{\partial \phi}{\partial x}(0, t)\delta_{\rm HP} \frac{\epsilon_{\rm s}}{\epsilon_{\rm HP}}
$$
\n(53)

mann boundary conditions specify the derivative of the variable, for example, $\frac{\partial}{\partial}$
dary conditions are a combination of Dirichlet and Neumann boundary conditions,
 $x = x_0$.

he reaction plane, designated as the coord

b_a (54) $\phi(x_{r},t)=0$

which are the Dirichlet boundary conditions, where n_{α}^b is the number density of particle α in the bulk solution.

$$
\exists (x, t) = 0
$$
\n
$$
\phi(x, t) = 0
$$
\n
$$
\phi(x, t) = 0
$$
\n
$$
\phi(x, 0) = n_{\alpha}^{b}
$$
\n(55)

\n(56)

\n(56)

\n
$$
n_{\alpha}(x, 0) = 0
$$
\n(57)

\nWe consider a proton-coupled electron transfer reaction, A + H⁺ + e⁻ \leftrightarrow B, occurring at the HP, with A and B

4th $\mathcal{H}^{\#}(J. Electrochem.)$ 2022, 28(2), 2108471 (15 of 30)
 $\phi(x_1,t) = 0$ (55)

which are the Dirichlet boundary conditions, where n_a^b is the number density of particle α in the bulk solution.

At $t = 0$, the initial c $\frac{d_1}{dx}(L)$ Electrochem.) 2022, 28(2), 2108471 (15 of 30)
 $\phi(x, t) = 0$ (55)

which are the Dirichlet boundary conditions, where n_a^b is the number density of particle α in the bulk solution.

At $t = 0$, the initial $w_r(t) = 0$
 $w_{r+1} = 0$ (55)
 $w_{r+1} = 0$ (55)
 $w_{r+1} = 0$ (55)
 $w_{r+1} = 0$, the initial conditions are shown as,
 $w_{r+1} = 0$, the initial conditions are shown as,
 $w_{r+1} = 0$, the initial conditions are shown as,
 w $+$ e - (55)

(55)

t density of particle α in the bulk solution.

(56)
 $+e^- \leftrightarrow B$, occurring at the HP, with A and B

cribed by the Frumkin-Butler-Volmer (FBV)

(58) $\phi(x, t) = 0$

(55)

which are the Dirichlet boundary conditions, where n_n^b is the number density of particle α in the bulk solution.

At $t = 0$, the initial conditions are shown as,
 $n_a(x, 0) = n_a^b$ (56)
 $\phi(x, 0) = 0$ equation $^{[55]}$, ,

$$
j = e_0 n_{\rm M} k_{00} \left(\frac{c_{\rm B,HP}}{c_{\rm B}^0} \exp\left(\frac{\alpha e_0 \eta}{k_{\rm B} T} \right) - \frac{c_{\rm A,HP}}{c_{\rm A}^0} \frac{c_{\rm H^*,HP}}{c_{\rm H^*}} \exp\left(- \frac{(1-\alpha)e_0 \eta}{k_{\rm B} T} \right) \right)
$$
(58)

 $\psi(k\neq \langle L \text{ Electrowe}kem) 2022, 28(2), 2108471 (15 of 30)$

which are the Dirichlet boundary conditions, where n_a^+ is the number density of particle α in the bulk solution.

An $L(t=0, \text{ the initial conditions are shown as},$
 $\phi(x,0) = n_a^b$ (56)
 $\phi(x,0) =$ $_1^2$ ⁻¹ for M(111) with (55)

ulk solution.

(56)

(57)

P, with A and B

-Volmer (FBV)

(58)

for M(111) with

eing the Planck

charge transfer

ectively. c_B^0 , c_A^0 $\Phi(k;\lambda) = 0$

which are the Dirichlet boundary conditions, where n_a ^h is the number density of particle α in the bulk solution.

At $t = 0$, the initial conditions are shown as,
 $n_a(x,0) = 0$ (55)

(66)
 $\phi(x,0) = 0$ (8 $T_{\text{corr}}\left(-\Delta G_a^{00}\right)$ with the inection \mathcal{L} $\frac{1}{h} \exp\left(-\frac{\Delta G_a^{00}}{k_B T}\right)$, with h being the Planck $k_{\rm B}T$, with *n* being the rialick

 $\pm \frac{\hbar^2 \pi}{L}$ *LEtectrochem.*) 2022, 28(2), 2108471 (15 of 30)

thoundary conditions, where n_e^b is the number density of particle α in the bulk solution

conditions are shown as,

on-coupled electron transfer reac the $\frac{1}{2}$ the $\frac{1}{2}$ (*S* = $\frac{1}{2}$ (*S*) (*S*) (59)

are Dirichlet boundary conditions, where *n_n*^b is the number density of particle *α* 6 (55)

of particle α in the bulk solution.

(55)

(57)

B, occurring at the HP, with A and B

y the Frumkin-Butler-Volmer (FBV)

(58)

culated by $(\sqrt{3} a_{\text{M}}^2)^{-1}$ for M(111) with
 $\left(-\frac{\Delta G_{\text{M}}^{(0)}}{k_{\text{B}}T}\right)$, w constant, $\Delta G_a^{\,\omega}$ the activation energy of the reaction at standard equilibrium state. α is the charge transfer (55)

Dirichlet boundary conditions, where n_a^* is the number density of particle α in the bulk solution.

initial conditions are shown as,

(66)

in the control compled electron transfer reaction, A + H⁺ + e⁻ +> $\frac{d_1\{c\neq c(f, Klectrochem.)\ 2022, 28(2), 2108471 (15 of 30)}{d(x,t)} = 0$
which are the Dirichlet boundary conditions, where n_n^b is the number density of particle α in the bull
At $t = 0$, the initial conditions are shown as,
 $n_a(x$ *Electrochem.*) 2022, 28(2), 2108471 (15 of 30)

15. (55)

16. (55)

17. It ansfer reaction, $A + H' + e^- \leftrightarrow B$, occurring at the HP, with A and B

16. (57)

17. It ansfer reaction, $A + H' + e^- \leftrightarrow B$, occurring at the HP, with A and (55)

ticle α in the bulk solution.

(56)

urring at the HP, with A and B

Frumkin-Butler-Volmer (FBV)

(58)

(58)

(58)

(59)

(59)

the charge transfer

at the HP, respectively. c_B^0 , c_A^0

tively. η is the ov coefficient, taken as 0.5. $c_{B,HP}$, $c_{A,HP}$ and $c_{H,HP}$ are the concentrations of B, A and H⁺ at the HP, respectively. c_B^0 , c_A^0 $, c_A^0$ 0 and c_{H}^{0} are the concentrations of B, A and H⁺ ur **EVALUATION 1989**
 EVALUATION 1992, 28(2), 2108471 (15 of 30)
 CVALUATION 100 (55)
 CVALUATION continual exponential of the parameteric exponential of the bulk solution.
 n_h^2
 n_h^3

(56)
 0

ansider a proton h_{em}) 2022, 28(2), 2108471 (15 of 30)

re n_a^b is the number density of particle α in the bulk solution.

(55)

er reaction, $A + H' + e^- \leftrightarrow B$, occurring at the HP, with A and B

reaction, *j*, is described by the Frumk $\phi(x_i, t) = 0$

which are the Dirichlet boundary conditions, where n_a ^b is the number density of particle

At $t = 0$, the initial conditions are shown as,
 $n_a(x, 0) = n_a$ ^b
 $\phi(x, 0) = 0$

We consider a proton-coupled elec che Direinlet boundary conditions, where n_a ⁿ is the number density of particle α in the bulk solution.

0, the initial conditions are shown as,

(56)

0

0 is the reaction potential of the reaction, $A + H^+ e^- \leftrightarrow B$, o (56)
 m_e^2 , the initial conditions are shown as,
 m_e^2 , m_e^2
 m_e^2
 (59)
 $\pi n_0^2 = n_a^2$
 $\pi n_0^2 = 0$

We consider a proton-coupled electron transfer reaction, $A + H^+ + e^- \leftrightarrow B$, occurring at the HP, with A and B

numer^{ical}, π solver, and the model using the creation, *i*, is described $\phi(x,0) = 0$

We consider a proton-coupled electron transfer reaction, A + H⁺ + e⁻ +> B, occurring at the HP, with A and B

being neutral species. The current density of the reaction, *j*, is described by the Frumkin-B

$$
\eta = \phi_{\rm M} - \phi_{\rm HP} - E^{00} \tag{59}
$$

where E^{00} is the equilibrium potential of the reaction under standard conditions, calculated by $E^{00} = -\Delta G^{0}/e_0$, $\frac{0}{a}$ with ΔG^0 being the Gibbs free energy under standard c

information.

mg neutral species. The current density of the reaction, *j*, is described by the Frumkin-Butler-Volmer (FBV)
 $e_6 n_a k_m \left[\frac{c_{80}}{c_0^5} \exp\left(\frac{n\sigma_c \eta}{k_B T}\right) - \frac{c_{20} \rho}{\epsilon_c^5} \frac{c_{12} \pi}{c_{11}} \exp\left(-\frac{(1-\alpha)\sigma_c \eta}{k_B T}\right) \right]$ (58 equation 168 , $\left(\frac{6 \text{ m/s}}{c_R^3} \exp\left(\frac{6 \text{ m/s}}{c_R^3} \right) - \frac{c_{GM}^2}{c_R^3} \exp\left(-\frac{(1-\alpha)c_0 \pi}{k_B T}\right)\right)$ (58)

where n_A is the areal number density of the electrode. For example, n_B is calculated by $(\sqrt{3} n_a)^3$ for M(11 $j = e_0 n_{\rm vt} k_{\rm m} \left(\frac{c_{\rm B} n}{c_{\rm B}} \exp\left(\frac{c_{\rm B} n}{c_{\rm B} n} \right) - \frac{c_{\rm A} n_{\rm s} c_{\rm B} n_{\rm s}}{c_{\rm B} n_{\rm s}} \right) = \frac{c_{\rm A} n_{\rm s} c_{\rm B} n_{\rm s}}{k_{\rm B} n_{\rm s}} \exp\left(- \frac{\Delta - \alpha_0 n_{\rm s}}{k_{\rm B} n} \right)$ (58)
where $n_{\rm A}$ is the areal num 00 where $n_{\rm d}$ is the area in the preservation of R_n is consumed. The $n_{\rm d}$ is consumed. The preserved of $\overline{R}_{\rm H}$ is equal to $\frac{k_{\rm B}T}{k_{\rm B}T}$ is $\left(n_{\rm d} \frac{Q_n}{k_{\rm B}}\right)^2$ for $\ln(111)$ with the lattice con where $n_{\rm B}$ is the areal number density of the electrode. For example, $n_{\rm B}$ is equelated by $(\sqrt{3} a_{\rm B}t)^2$ for M(111) with
the lattice constant $a_{\rm B}$. The pre-exponential factor $k_{\rm B}$ is equal to $\frac{k_B T}{h_B T$ the lattice constant a_{bb} . The pre-exponential factor k_{eq} is equal to $\frac{k_{q}T}{n}$ exp $\left[-\frac{\Delta G_{eq}^{(0)}}{k_{B}T}\right]$, with h being the Pla
constant, $\Delta G_{e}^{(0)}$ the activation energy of the reaction at standard equilibr factor k_{ω} is equal to $\frac{k_{B}T}{\hbar}$ exp $\left[-\frac{\Delta C_{\omega}^{(0)}}{k_{B}T}\right]$, with *h* being the Planck
e reaction at standard equilibrium state. α is the charge transfer
are the concentrations of B, A and H⁺ at the HP, constant, $\Delta G_{\nu}^{(m)}$ the activation energy of the reaction at standard equilibrium state. α is the charge transfer coefficient, taken as 0.5. c_{mu} oc_{tur} and c_{mu} are the concentrations of B, A and H at t constant, ΔC_{ν}^{m} the environment occurs of the reaction at stundard equivablent meats. α is the enarge transfer α_{ν}^{m} are the concentrations of B, A and H' under standard conditions, respectively. η is t coefficient, taken as 0.5. c_{min} e c_{out} and c_{min} are the concentrations of B, A and H at the HP, respectively. c_B , c_A , c_A and $m = b_B$, $p = b_B$ and $p = b_B$ and $p = b_B$ and $m = b_B$ and $p = b_B$ are concentrations and ω_n ² are the concentrations of B, A and H² under standard conditions, respectively. η_1 is the overpotential,
 $\eta = \phi_N - \phi_{00} - E^{\alpha}$

where E^{α} is the equilibrium potential of the reaction under standard the ϵ ^b₀ ϵ - ϵ ⁰ ϵ - ϵ $\eta = \phi_0 - e^{-\beta v}$, when the assumption and the reaction under standard conditions, calculated by $E^{\alpha} = -\Delta C^{\alpha}v_c$, with ΔC^2 being the Gibbs free energy under standard conditions.

We numerically solve the model using tion with ϕ_{Ms} and the distributions of the concentration of A, c_{As} at 0.1 s, 1 s and 5 s of the EDL is 100 μ m, and the time duration is 5 s. The steady current density is taked with reading responsed. The We numerically solve the model using the built-in partial differential equations solver, pdepe function, in Matahob, with the parameters listed in Table 1. Mataho script of this model is provided in the supporting informa Matlab, with the parameters listed in Table 1. Matlab script of this model is pro

The typical results of the PNP equation are shown in Figure 8, including the steat

The typical results of the PNP equation are shown in F on of B at the HP. When $\phi_M \le E^m$, the reduction reaction occurs. As the clectric potential decreases,
then the stimal of the diffusion limiting current, which is limited by the low concentration
HP. From Figure 8(B), threation with δ_{bs} and the distributions of the concentration of $\Lambda_{t} \propto_{s}$ at 0.1 s, 1 s and 5 s at 0.4 v_{an} The spatial
trange of the EDL is 100 µm, and the time duration is 5 s. The steady eurrent density is ta c_A , at 0.1 s, 1 s and 5 s at 0.4 V_{SHE}. The spatial
dy current density is taken at 5 s. As $\phi_M > E^{\omega}$,
ensity increases near exponentially in the low
gion when $\phi_M > 0.7$ V_{SHE}, caused by the low
tion occurs. As the , 1 s and 5 s at 0.4 V_{SHE}. The spatial
density is taken at 5 s. As $\phi_M > E^0$,
ases near exponentially in the low
 $\phi_M > 0.7$ V_{SHE}, caused by the low
As the electric potential decreases,
is limited by the low concentrat range of the EDL is 100 μ m, and the time duration is 5 s. The steady current density is taken at 5 s. As ϕ , the society decomocours and B is consumed. The current density is taken at 5 s. As ϕ , overeptential regi gion and transitions to the diffusion limiting region when $\phi_M > 0.7 \text{ V}_{\text{SIE}}$, caused

B at the HP. When $\phi_M \leq E^0$, the reduction reaction occurs. As the electric potential

ity increases and reaches the diffusion li

$$
\frac{\partial}{\partial x}\left(\epsilon_s \frac{\partial \phi}{\partial x}\right) = -e_0 \Sigma z_\alpha n_\alpha \tag{60}
$$

and reaches almost zero at the HP, signifying diffusion limiting effects.
\nThen we apply some approximations to reduce the modified PNP equation back to the classical PNP
\nequation. Firstly, under the assumption
$$
n_{\alpha^*} \ll n_{\alpha}
$$
, Eq. (35) is simplified as,
\n
$$
\frac{\partial}{\partial x} \left(\epsilon_s \frac{\partial \phi}{\partial x} \right) = -e_0 \sum z_{\alpha} n_{\alpha}
$$
\n(60)
\nAs for the modified Nernst-Planck equation, neglect of the asymmetric steric effects, that is, $\gamma_i = 1$, simplifies
\nEq. (51) to,
\n
$$
\frac{\partial n_{\alpha}}{\partial t} = \frac{\partial}{\partial x} \left(D_{\alpha} \frac{n_s}{n_t} \frac{\partial n_{\alpha}}{\partial x} + D_{\alpha} \frac{n_{\alpha}}{n_t} \sum_{i \neq s} \frac{\partial n_i}{\partial x} + D_{\alpha} \beta \frac{n_{\alpha} n_s}{n_t} z_{\alpha^0} \frac{\partial \phi}{\partial x} \right)
$$
\n(61)
\nFurthermore, if the electrolyte is sufficiently dilute, that is, $n_{\alpha} \ll n_t$, and $n_t \approx n_s$ the expression is returned back to
\nthe classical Nernst-Planck equation,
\n
$$
\frac{\partial n_{\alpha}}{\partial t} = \frac{\partial}{\partial x} \left(D_{\alpha} \frac{\partial n_{\alpha}}{\partial x} + D_{\alpha} \beta n_{\alpha} z_{\alpha^0} \frac{\partial \phi}{\partial x} \right)
$$
\n(62)
\n(62)

$$
\frac{\partial n_{\alpha}}{\partial t} = \frac{\partial}{\partial x} \left(D_{\alpha} \frac{\partial n_{\alpha}}{\partial x} + D_{\alpha} \beta n_{\alpha} z_{\alpha} e_0 \frac{\partial \phi}{\partial x} \right) \tag{62}
$$

 $\phi_{\text{pe}}(N_{\text{err}})$ 0.3
 $\phi_{\text{pe}}(N_{\text{err}})$ 5.5
 $n_{\text{A}}(m^2)$ 4.713 × 10³ Latrice constant of the electrode
 $n_{\text{A}}(m^2)$ Equilibrium perpension of the electrode
 $\Delta C_{\text{e}}^{30}(\text{V})$ 0.6
 $\Delta C_{\text{e}}^{30}(\text{V})$ 0.6
 based on the electroster of the electrode Estimated $n_{\alpha}(m^{+})$
 $n_{\alpha}(m^{+})$
 $A \cdot 713 \times 10^{18}$
 Exercity may become in the electrode $\Delta C_{\alpha}^{m}(\mathbf{v})$
 Exercity may become in the electron of the reaction at standa n_{off} and n_{off} and n_{off} and n_{off} and n_{off} and n_{off} becausing of $M(111)$, calculated by $(\sqrt{3} \alpha_n)^4$

Reaction properties
 $\Delta C_n^M(\mathbf{v})$ 0.4 **and in the impedance response of the reserion at** Example the ENL of the ENL of the EDL. We recommend the readers of the readers to follow the reader of the reader of the reader of the readers to studiate the reader of the readers to $\Delta G_n^{\text{eff}}(eV)$ 0.4 Equilibrium stat Equilibrium perturbation energy of the reaction at standard state
 $E^{\text{P}}(Y_{\text{val}})$ 0.6

At equilibrium state, that is $f_a = 0$, Eq. (62) turns into Eq. (3), the Boltzmann equation. Similarly, when $f_a = 0$,

Eq. (61) tur

ing.

Example 1.1
 Example 1.1
 Example 1.1
 Example 1.1
 Example 1.2
 Example 1. EXECUTE: $\frac{1}{6}$ and $\frac{1}{6}$ and $\frac{1}{3}$ and **Figure 8** Typical results of the PNN is observation of $\frac{1}{65}$ and $\frac{1}{165}$ and $\frac{1}{$ **Figure 8** Typical results of the PNP theory, including the current density varying with the electrode potential, and the distributions
of the concentration of A at 0.1 s, 1 s and 5 s at 0.4 V_{zr}. The spotial range for c **Figure 8** Typical results of the PNP theory, including the current density varying with the electrode potential, and the distributions
of the concentration of A at 0.1 s, 1 s and 5 s at 0.4 V_m. The spatial range for ca of the concentration of A at 0.1 s, 1 s and 5 s at 0.4 V_{rem}. The spatial range for eacteduation is 100 pm from the IIP, and the time duration for calculation is 5 s. The parameters for calculation are listed in Table 1. tion for calculation is 5 s. The parameters for calculation are listed in Table 1. Matlab script of this model is provided in the support-
ing information.

and appreciate the beauty of physicochemical processes

in the F There are usually three physicochemical processes

in the EDL: double-layer charging, charge transfer

reactions, and diffusion. The double-layer charging

involves redistribution of ions in the EDL, namely,

involves red

 $\begin{array}{ll}\n\text{a.2} & \bullet_{M} = 0.4 \text{ V}_{\text{SHE}} \\
\hline\n\text{b.3} & \bullet_{M} = 0.4 \text{ V}_{\text{SHE}} \\
\hline\n\text{m} & \times f(\mu \text{m})\n\end{array}$

express to $\pi/(\mu \text{m})$

matity varying with the electrode potential, and the distributions

range for calculation is $\frac{\phi_M = 0.4 \text{ V}_{\text{SHE}}}{20}$
 $\frac{\phi_M = 0.4 \text{ V}_{\text{SHE}}}{40}$
 $\frac{\pi}{100}$
 $\frac{\pi}{100}$
 $\frac{\pi}{100}$ and the distributions

range for calculation is 100 μ m from the HP, and the time dura-

Table 1. Matlab script of this mod $\frac{6}{\cancel{6}}$ $\frac{20}{\cancel{20}}$ $\frac{40}{\cancel{60}}$ $\frac{60}{\cancel{60}}$ $\frac{80}{\cancel{60}}$ $\frac{100}{\cancel{60}}$
 $\frac{x}{f(\mu m)}$

Ensity varying with the electrode potential, and the distributions

ange for calculation is 100 μ m from the HP, and $x/(µm)$

sisty varying with the electrode potential, and the distributions

range for calculation is 100 $µm$ from the HP, and the time dura-

Table 1. Matlab script of this model is provided in the support-
 c_{d}
 c_{d lution.

ing information.

and appreciate the beauty of physicochemical modell-

img.

There are usually three physicochemical processes

The metallicare charging throube-layer charging through the EDL, namely,

the EDL: double-la and appreciate the beauty of physicochemical modell-

ing.

There are usually three physicochemical processes

in the EDL: double-layer charging, charge transfer

involves redistribution of ions in the EDL, under the

inv and appreciate the beauty of physicochemical modell-

There are usually three physicochemical processes

in the EDL: double-layer charging, charge transfer

recordions, and diffusion. The double-layer charging

change of There are usually three physicochemical processes

The FDL: double-layer charging, charge transfer

reactions, and diffusion. The double-layer charging

involves redistribution of ions in the EDL, namely,

the Henric doub the EDL: double-layer charging, charge transfer

recions, and diffusion. The double-layer charging

reloves redistribution of ions in the EDL, materly,

mapp of the net charge stored in the EDL, under the

range of the ne reactions, and diffusion. The double-layer charging involves redistribution of ions in the EDL, namely,
involves redistribution of ions in the EDL, namely,
the precedent of the electric potential. As the EDL is usually pr

involves redistribution of ions in the EDI, namely,
charge of the net charge stored in the EDL, inder the conscious constrol the double-layer charge
of the clectric potential. As the EDL is usually
process, R_0 is a res change of the net charge stored in the FDL, under the **Figure 9** ECM in the electrochement system. C_4 is an inter-
control of the electric potential. As the EDL is usually
control of the electric potential. As the EDL control of the electric potential. As the FDL is usually and expectate, as a secision of a low nanometric thick, ion transport in the EDL and process, W_i is a resistance, associated with the charge transfer is often to only a few nanometers thick, ion transport in the EDL

reactions process, N describes the diffusion of species molecled

is often considered to be completed inmediately.

Therefore, charging the EDL is equivalent to cha is often considered to be completed immediately.

in the charge transfer reactions, *R*, is the electrodyie sultimorean

an interfacial capacitance *C_s*. As for the charge

animetrical capacitance *C_s*. As for the cha enciore, charging the EDL is equivalent to charging
instance, associated with the migration pocass in the balk so-
instehrated capacitance C_{α} . As for the charge
for reactions, it takes less than 1 ps for an
tron to t

 $\mathcal{L}\#(L\text{ }Electrochem.)$ 2022, 28(2), 2108471 (18 of 30)

mathematical tool—Fourier transform—will be introduced. Then, we will work on calculating the impedance

response of a basic ECM to express the working mechanism of Fou t \pm *k\\\thetrochem.*) 2022, 28(2), 2108471 (18 of 30)

mathematical tool—Fourier transform—will be introduced. Then, we will work on calculating the impedance

response of a basic ECM to express the working mechanism more than a specific kind of classical electrochemical techniques. It provides a powerful mathematical physics **EDENT THE ELECT THE ELECT CONDENTIAL ELECT CONDENTIAL (Solve the electrochemical tool—Fourier transform—will be introduced. Then, we will work on calculating the impedance
response of a basic ECM to express the working m** $\exists \ell \neq (J. Electrochem.) 2022, 28(2), 2108471 (18 of 30)$
 Example 11.1 Basic contrastions in the introduced. Then, we will work on calculating

response of a basic ECM to express the working mechanism of Fourier transform. Reader $\frac{E(E \neq (I, Electrochem.) 2022, 28(2), 2108471 (18 of 30)}{E(1 + 10)}$

Suppose of a basic ECM to express the working mechanism of Fourier transform. Readers may find that EIS is

prove than a specific kind of classical electrochemical t th ($k \neq (J. Electrochem.)$ 2022, 28(2), 2108471 (18 of 30)
mathematical tool—Fourier transform—will be introduced. Then, we will work on calculatin
response of a basic ECM to express the working mechanism of Fourier transform. Re $# \ell \neq (J. Electrochem.) 2022, 28(2), 2108471 (18 of 30)$ mathematical tool—Fourier transform—will be introduced. Then, we will work on calcular

response of a basic ECM to express the working mechanism of Fourier transform. Readers
 $\frac{dE\mathcal{L}(E|E|curochem, 2022, 28(2), 2108471 (18 of 30))}{dE\mathcal{L}(E|E|curochem, 2022, 28(2), 2108471 (18 of 30))}$

atthermatical tool—Fourier transform—will be introduced. Then, we will work on calculating the impedance

sponse of a basic ($\frac{1}{2}$ + (*K* $\frac{1}{r}$)= $\frac{1}{2}$ + (*K* $\frac{1}{r}$) + (*K* $\frac{1$ **HEP:** (*LEhermochem.*) 2022, 28(2), 2108471 (18 of 30)

mathematical tool—Fourier transform—will be introduced. Then, we will work on calculating the impedance

response of a basic ECM to express the vorbing mechanism of $\#E \neq (L \tElectrochem.) 2022, 28(2), 2108471 (18 of 30)$

mathematical tool—Fourier transform—will be introduced. Then, we will work

response of a basic ECM to express the working mechanism of Fourier transform

more than a spec (Ferman 100) = $\int_{-\infty}^{\infty} f(t) \exp(j\omega t) d\omega$

(Ferman 1 = $\int_{-\infty}^{\infty} f(t) \exp(j\omega t) d\omega$ = $\int_{-\infty}^{\infty} f(t) \exp(-j\omega t) d\omega$ = $\int_{-\infty}^{\infty} f(t) \exp(-j\omega t) d\omega$

(Factor of a basic ECM to express the working mechanism of Fourier transf $\frac{dE}{dt}$ (*L Electrochem.*) 2022, 28(2), 2108471 (18 of 30)

mathematical tool—Fourier transform—will be introduced. Then, we will work on calculating the intersponse of a basic ECM to express the working mechanism 电化学(*J. Electrochem.*) 2022, 28(2), 2108471 (18 of 30)
ansform—will be introduced. Then, we will work on calculating the impedance
press the working mechanism of Fourier transform. Readers may find that EIS is
lassical el

$$
F(\omega) = \mathcal{F}(f(t)) = \int_{-\infty}^{\infty} f(t) \exp(-j\omega t) dt
$$
\n(63)

$$
f(t) = \mathcal{F}^{-1}(F(\omega)) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) \exp(j\omega t) d\omega
$$
\n(64)

mathematical tool—Fourier transform—will be introduced. We will work on calculating the impedance response of a basic ECM to express the working mechanism of Fourier transform. Readers may find that EIS is more than a specific kind of classical electrochemical techniques. It provides a powerful mathematical physics approach to solve the electrochemical problems and represents a different look at electrochemical problems. **S.1** Basis of EIS, including the Fourier transform and the example of a simple electrical circuit.
$$
S.1.1
$$
 Fourier transform of a function $f(t)$ is, $F(\omega) = \pi f(t)\cos(\pi t)$. Therefore, $F(\omega) = \pi f(t)\cos(\pi t)$ and $F(\omega) = \pi f(t)\cos(\pi t)$. $F(\omega) = \pi f(t)\cos(\pi t)$ and $F(\omega) = \pi f(t)\cos(\pi t)$. $F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(t)\cos(\pi t) dt$. $F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) \exp(j\omega t) d\omega$ (64) derived from Eq.(63) as follows, $F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) \exp(j\omega t) d\omega = \int_{-\infty}^{\infty} F(\omega') \exp(j\omega t) d\omega = F(\omega)$ (65) where we have used the Dirac's delta function $\delta(\omega - \omega') = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega') \delta(\omega - \omega') d\omega = F(\omega)$ (65) where we have used the Dirac's delta function $\delta(\omega - \omega') = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-j\omega t) d\omega = F(\omega)$ (66) where we have used the Dirac's delta function $\delta(\omega - \omega') = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-j\omega t) d\omega = F(\omega)$ (66) where we have used the Dirac's delta function $\delta(\omega - \omega') = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-j\omega t) d\omega = F(\omega)$ (66) where we have used the Dirac's delta function $\delta(\omega - \omega') = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-j$

 $\frac{1}{2\pi}$ $\int_{-\infty}^{\infty} \exp(-j(\omega-\omega')t)dt$.

$$
\mathcal{F}\left(\frac{\mathrm{d}^n f(t)}{\mathrm{d}t^n}\right) = (j\omega)^n F(\omega) \tag{66}
$$

$$
\mathcal{F}\left(\frac{df(t)}{dt}\right) = \int_{-\infty}^{\infty} f'(t) \exp(-j\omega t) dt = f(t) \exp(-j\omega t) \Big|_{-\infty}^{\infty} + j\omega \int_{-\infty}^{\infty} f(t) \exp(-j\omega t) dt = j\omega F(\omega)
$$
(67)

$$
\mathcal{F}(f(t)^*g(t)) = F(\omega)G(\omega) \tag{68}
$$

where the sign "*" denotes the convolution operator defined as
$$
f(t)^*g(t) = \int_{-\infty}^{\infty} f(\tau)g(t-\tau)d\tau
$$
, $F(\omega)$ and $G(\omega)$

$$
\frac{1}{2\pi} \int_{-\infty}^{\infty} t(\omega) \left| \int_{-\infty}^{\infty} \exp(-t(\omega - \omega t)) \right| d\omega = \int_{-\infty}^{\infty} t(\omega) t(\omega - \omega t) \cdot d\omega = t(\omega)
$$
\nwhere we have used the Dirac's delta function $\delta(\omega - \omega') = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-j(\omega - \omega' t)) dt$.
\nElectrochemical processes are usually described by ordinary or partial differential equations. Therefore, the Fourier transform of the *n*th derivative of a function is useful,
\n
$$
\int \left(\frac{d^2f(t)}{dt^2}\right) = (j\omega)^n F(\omega)
$$
\n(66)
\ngiven that $f^{(n-1)}(t) = 0$ at the initial state.
\nWe prove for the case $n = 1$,
\n
$$
\int \left(\frac{d^2f(t)}{dt}\right) = \int_{-\infty}^{\infty} f'(t) \exp(-j\omega t) dt = f(t) \exp(-j\omega t) \Big|_{-\infty}^{\infty} + j\omega \int_{-\infty}^{\infty} f(t) \exp(-j\omega t) dt = j\omega F(\omega)
$$
\n(67)
\nwhere we use the natural boundary conditions, $f(\infty) = f(-\infty) = 0$. The case of other orders can be proved by re-
\npearing the manipulation of Eq.(67).
\nAnother often-used property of Fourier transform is the convolution theorem,
\n
$$
\mathcal{F}(f(t)^* g(t)) = F(\omega)G(\omega)
$$
\n(68)
\nwhere the sign u^* denotes the convolution operator defined as $f(t)^* g(t) = \int_{-\infty}^{\infty} f(\tau) g(t - \tau) d\tau$, $F(\omega)$ and $G(\omega)$
\ndenote the Fourier transform of $f(t)$ and $g(t)$, respectively. Eq. (68) is proved as follows,
\n
$$
\mathcal{F}(f(t)^* g(t)) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\tau) g(t - \tau) d\tau \exp(-j\omega t) dt = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\tau) e^{-j\omega t - \tau} d\tau dt
$$
\n[67] The *j*th

sess are usually described by ordinary or partial differential equations. Incretore, the

derivative of a function is useful,
 (66)
 e initial state.
 $= 1$,
 $\omega f/dc = f(t)exp(-j\omega)\int_{-\infty}^{\infty} i^2\omega \int_{-\infty}^{\infty} f(t)exp(-j\omega)dt = j\omega$ $\mathcal{F}\left(\frac{d^h f(t)}{dt^h}\right) = (j\omega)^h f(\omega)$
 $\mathcal{F}\left(\frac{d^h f(t)}{dt}\right) = (j\omega)^h f(\omega)$
 $\mathcal{F}\left(\frac{d f(t)}{dt}\right) = \int_{-\infty}^{\infty} f'(i) \exp(-j\omega t) dt = f(t) \exp(-j\omega t) \int_{-\infty}^{\infty} f(t) \exp(-j\omega t) dt = j\omega F(\omega)$

where we use the natural boundary conditions, $f(x) = f(-\$ For $\frac{d\vec{a}e^{-\vec{b}}}{dt}$ = $\int -Q\omega pT(\omega)$ (60)

con that $\omega^{(n-1)}(0) = 0$ at the initial state.

We prove for the case $n = 1$,
 $\frac{d\vec{f}(t)}{dt} = \int_{-\infty}^{\infty} f'(0) \exp(-j\omega t) dt = f(t) \exp(-j\omega t) \int_{-\infty}^{\infty} f(0) \exp(-j\omega t) dt = j\omega f(\omega)$ (67)
 given that $f^{\omega_0}(t) = 0$ at the initial state.

We prove for the case $n = 1$,
 $\pi \int \frac{df(t)}{dt} = \int_{-\infty}^{\infty} f'(t) \exp(-j\omega t) dt = f(t) \exp(-j\omega t) \int_{-\infty}^{\infty} f(t) \exp(-j\omega t) dt = j\omega F(\omega)$ (67)
 $\omega t = \omega$ the the antaral boundary conditions, f We prove for the case $n = 1$,
 $g\left(\frac{df(t)}{dt}\right) = \int_{-\infty}^{\infty} f'(v)exp(-j\omega t)dt = f(t)exp(-j\omega t)\int_{-\infty}^{\infty} + j\omega \int_{-\infty}^{\infty} f(t)exp(-j\omega t)dt = j\omega f(\omega)$ (67)

where we use the natural boundary conditions, $f(\infty) = f(-\infty) = 0$. The case of other o $\mathcal{F}\left(\frac{df(t)}{dt}\right) = \int_{-\infty}^{\infty} f'(t) \exp(-j\omega t) dt = f(t) \exp(-j\omega t) \int_{-\infty}^{\infty} f(t) \exp(-j\omega t) dt = j\omega F(\omega)$
where we use the natural boundary conditions, $f(\infty) = f(-\infty) = 0$. The case of other orders can be
peating the manipulation of Eq.(6

 $Z(\omega) = \frac{\mathcal{F}(V(t))}{\mathcal{F}(i(t))}$

A simple ECM is shown in Figure 10(A), which consists of two resistors and one potential of this circuit is,
 $V_{\text{tot}}(t) = V_1(t) + V_2(t)$ $\frac{V(t)}{V(t)}$ (70) $\text{tr}\{\{\frac{\omega}{2}(L \text{ } \text{Electrochem.})\ 2022, 28(2), 2108471 \ (19 \text{ of } 30)\}\$
 ω) = $\frac{\mathcal{F}(V(t))}{\mathcal{F}(i(t))}$ (70)

A simple ECM is shown in Figure 10(A), which consists of two resistors and one capacitor. The total electric

tential 电化学(*J. Electrochem.*) 2022, 28(2), 2108471 (19 of 30)
(70)
igure 10(A), which consists of two resistors and one capacitor. The total electric

$$
V_{\text{tot}}(t) = V_1(t) + V_2(t)
$$
\nwhere

$$
\frac{\text{#}\{\ell\}^{\omega}(J. Electrochem.) 2022, 28(2), 2108471 (19 of 30)}
$$
\n
$$
Z(\omega) = \frac{\sigma(V(t))}{\sigma(i(t))}
$$
\n(A simple ECM is shown in Figure 10(A), which consists of two resistors and one capacitor. The total electric potential of this circuit is,
\n
$$
V_{\text{tot}}(t) = V_1(t) + V_2(t)
$$
\nwhere
\n
$$
V_1(t) = R_0 i(t), i(t) = \frac{V_2(t)}{R} + C \frac{dV_2(t)}{dt}
$$
\nApplying Fourier transform into Eqs. (71) and (72), we obtain,
\n
$$
\sigma(V_{\text{tot}}(t)) = \sigma(V_1(t)) + \sigma(V_2(t))
$$
\n
$$
\sigma(V_{\text{tot}}(t)) = \sigma(V_1(t)) + \sigma(V_2(t))
$$
\n(73)
\n
$$
\sigma(V_1(t)) = R_0 \sigma(i(t)), \sigma(i(t)) = \frac{\sigma(V_2(t))}{R} + j\omega C \sigma(V_2(t)).
$$
\n(74)
\nCombining Eqs. (70) and (74), the electrochemical impedance reads,
\n
$$
Z = \frac{\sigma(V_{\text{tot}}(t))}{R} = R_1 + \frac{R}{t}
$$
\n(75)

$$
\mathcal{F}(V_{\text{tot}}(t)) = \mathcal{F}(V_1(t)) + \mathcal{F}(V_2(t))
$$
\n⁽⁷³⁾

$$
\mathcal{F}(V_1(t)) = R_0 \mathcal{F}(i(t)), \mathcal{F}(i(t)) = \frac{\mathcal{F}(V_2(t))}{R} + j\omega C \mathcal{F}(V_2(t)).
$$
\n(74)

$$
\mathcal{Z}(\omega) = \frac{\mathcal{F}(V(t))}{\mathcal{F}(i(t))}
$$
\n
$$
Z(\omega) = \frac{\mathcal{F}(V(t))}{\mathcal{F}(i(t))}
$$
\n
$$
(\mathcal{F}(t))
$$
\n
$$
V_{\text{out}}(t) = V_1(t) + V_2(t)
$$
\n
$$
V_{\text{out}}(t) = V_1(t) + V_2(t)
$$
\nwhere\n
$$
V_1(t) = R_{\theta}(t), i(t) = \frac{V_2(t)}{R} + C \frac{dV_2(t)}{dt}
$$
\n
$$
(\mathcal{F}(t)) = \frac{V_1(t)}{R} + C \frac{dV_2(t)}{dt}
$$
\n
$$
(\mathcal{F}(t)) = \frac{V_2(t)}{R} + C \frac{dV_2(t)}{dt}
$$
\n
$$
(\mathcal{F}(t)) = \frac{V_1(t)}{R} + \frac{V_2(t)}{dt}
$$
\n
$$
(\mathcal{F}(t)) = \frac{V_1(t)}{V_1(t)} + \frac{V_1(t)}{V_2(t)}
$$
\n
$$
(\mathcal{F}(t)) = \frac{V_1(t)}{R} + j\omega C \mathcal{F}(V_2(t)).
$$
\n
$$
(\mathcal{F}(t))
$$
\n
$$
(\mathcal{F}(
$$

$$
Z'(\omega) = R_0 + R \frac{1}{1+(\omega \tau)^2} \tag{76}
$$

$$
Z''(\omega) = -R \frac{\omega \tau}{1 + (\omega \tau)^2} \tag{77}
$$

$$
|Z| = \sqrt{(Z')^2 + (Z'')^2} = \sqrt{R_0^2 + \frac{R^2 + 2RR_0}{1 + (\omega \tau)^2}}
$$
(78)

¹ A simple Let II is shown in Figure 16(1), which contains 51 cm because of the Laplacelet. The total electric
\npotential of this circuit is,
\n
$$
V_w(t) = V_1(t) + V_2(t)
$$
 (71)
\nwhere
\n
$$
V_1(t) = R_0(t), i(t) = \frac{V_2(t)}{R} + C \frac{dV_2(t)}{dt}
$$
 (72)
\nApplying Fourier transform into Eqs. (71) and (72), we obtain,
\n
$$
\mathcal{F}(V_w(t)) = \mathcal{F}(V_1(t)) + \mathcal{F}(V_2(t))
$$
 (73)
\n
$$
\mathcal{F}(V_1(t)) = R_0 \mathcal{F}(i(t), \mathcal{F}(i(t)) = \frac{\mathcal{F}(V_2(t))}{R} + j\omega C \mathcal{F}(V_2(t))
$$
 (74)
\nCombining Eqs. (70) and (74), the electrochemical impedance reads,
\n
$$
Z = \frac{\mathcal{F}(V_w(t))}{\mathcal{F}(i(t))} = R_0 + \frac{R}{1 + j\omega RC}
$$
 (75)
\nThe real part, $Z'(\omega)$, and the imaginary part, $Z'(\omega)$, of Eq. (75) are,
\n
$$
Z'(\omega) = R_0 + R \frac{1}{1 + (\omega \tau)^2}
$$
 (76)
\n
$$
Z''(\omega) = -R \frac{\omega \tau}{1 + (\omega \tau)^2}
$$
 (77)
\nwhere $\tau = RC$ is the time constant of this circuit. The amplitude and phase angle of this impedance are,
\n|Z| = $\sqrt{(Z')^2 + (Z'')^2} = \sqrt{R_0^2 + \frac{R^2 + 2RR_0}{1 + (\omega \tau)^2}}$ (78)
\n φ = arctanh $(\frac{Z'}{Z'})$ = -arctanh $(\frac{R\omega \tau}{R + R_0(1 + (\omega \tau)^2)})$ (79)
\nFigure 10(19) shows the EIS of the *R* (and *R*), and the high-frequency interest, on the horizontal axis is equal to *R*.

 $V_1(t) = R_{\theta}(t), i(t) = \frac{V_2(t)}{R} + C \frac{dV_2(t)}{dt}$

Applying Fourier transform into Eqs. (71) and (72), we obtain,
 $\mathcal{F}(V_{\text{ss}}(t)) = \mathcal{F}(V_1(t)) + \mathcal{F}(V_2(t))$
 $\mathcal{F}(V_1(t)) = R_{\theta}\mathcal{F}(i(t)), \mathcal{F}(i(t)) = \frac{\mathcal{F}(V_2(t))}{R} + j\omega C \mathcal{F}(V_2(t$ Eqs. (70) and (74), the electrochemical impedance reads,

(b)) = $R_0 + \frac{R}{1 + i\omega RC}$
 $\Rightarrow R_0 + \frac{R}{1 + i\omega RC}$
 $\Rightarrow R = \frac{P_0 + \frac{R}{1 + i\omega RC}}{P_0 + i\omega r}$
 $\Rightarrow R = \frac{P_0 + \frac{R}{1 + i\omega r}}{P_0 + i\omega r}$
 $\Rightarrow R = \frac{P_0 + \frac{R}{1 + i\omega r}}{P_0 + i\omega r}$
 \Rightarrow 蓸 蔀 (79) Applying Fourier transform into Eqs. (71) and (72), we obtain,
 $V_m(t) = \pi (V_m(t)) + \pi (V_s(t))$ (73)
 $V_r(t) = R_0 \pi (t) (t) + \pi (V_s(t))$ (74)
 $V_r(t) = R_0 \pi (t) (t)$ and (74) , the electrochemical impedance reads,
 $\frac{\sigma}{\pi} (V_m(t)) = R_0 + \frac{R}{1+i$ A growing rounter armstorm municipal content is equal to R and the high-frequency intercept on the Frequency intercept on the semi-circle is equal to R and the high-frequency intercept on the higher of this impediate are $\mathcal{F}(V_1(t)) = R_0 \mathcal{F}((t))$, $\mathcal{F}(V_2(t)) = \frac{\mathcal{F}(V_3 \times t)}{R} + j\omega C \mathcal{F}(V_2(t))$. (74)

Combining Eqs. (70) and (74), the electrochemical impedance reads,
 $Z = \frac{\mathcal{F}(V_3 \times t)}{\mathcal{F}(t)} = R_0 + \frac{R}{1+j\omega RC}$ (75)

The real part, $Z'(\$ Combining Eqs. (70) and (74), the electrochemical impedance reads,
 $Z = \frac{\mathcal{F}(V_{\text{tot}}(t))}{\mathcal{F}(t)} = R_0 + \frac{R}{1 + \mu_0 RC}$ (75)

The real part, $Z'(\omega)$, and the imaginary part, $Z'(\omega)$, of Eq. (75) arc,
 $Z(\omega) = R_0 + R \frac{1}{1 + (\omega r)^$ $Z = \frac{\nabla f'(x_0)}{\nabla f(x_0)} = R_0 + \frac{R}{1 + i\omega R G}$ (75)

The real part, $Z'(\omega)$, and the imaginary part, $Z'(\omega)$, of Eq. (75) are,
 $Z'(\omega) = R_0 + R \frac{1}{1 + i(\omega T)^2}$ (76)
 $Z'(\omega) = -R_0 + \frac{1}{1 + i(\omega T)^2}$ (77)

where $\tau = RC$ is the time con $Z = \frac{N_{\text{tot}}(V)}{T(i(t))} = R_0 + \frac{N_{\text{tot}}(V)}{1 + i_0 R C}$ (75)

The real part, $Z'(\omega)$, and the imaginary part, $Z'(\omega)$, of Eq. (75) are,
 $Z'(\omega) = -R_0 + R \frac{1}{1 + (\omega \tau)^2}$ (76)
 $Z'(\omega) = -R \frac{\omega \tau}{1 + (\omega \tau)^2}$ (77)

where $\tau = RC$ is the t The real part, $Z'(\omega)$, and the imaginary part, $Z'(\omega)$, of Eq. (75) are,
 $Z'(\omega) = R_5 + R \frac{1}{1+(\omega\tau)^3}$ (76)
 $Z'(\omega) = -R_5 + R \frac{1}{1+(\omega\tau)^3}$ (77)

where $\tau = RC$ is the time constant of this circuit. The amplitude and phase angl (o) = $R_0 + R_1$ (76)

(a) = $- R_1$ Ti(ar)² (77)

(a) = $- R_1$ Ti(ar)² (a) = $- R_2$ (is the time constant of this circuit. The amplitude and phase angle of this impedance are,
 $-\sqrt{(Z')^2 + (Z')^2} = \sqrt{R_0^2 + \frac{R^2 + 2RR_0}{1 + (\$ where $\tau = RC$ is the time constant of this circuit. The amplitude and phase angle of this impedance are,
 $|Z| = \sqrt{(Z')^2 + (Z')^2} = \sqrt{R_0^2 + \frac{R^2 - 2RR_0}{1 - 6R\sigma^2}}$ (78)
 $\varphi = \arctanh\left(\frac{Z'}{Z'}\right) = -\arctanh\left(R_0 + R_0R_0/R_0$

Figure 10 $|Z| = \sqrt{(Z')^{2}+(Z')^{2}} = \sqrt{(R_{\phi}^{2}+R_{\phi}^{2}+2R_{\phi}^{2})}$ (78)
 $\varphi = \arctanh\left(\frac{Z'}{Z'}\right) = -\arctanh\left(R_{\phi} + R_{\phi}(R/\psi)\right)$ (79)

Figure 10(B) shows the EIS of the $R_{\phi}(R/\psi C)$ circuit in the Nyquist plot, which is a perfect semi-circle. (78)

(79)

olot, which is a perfect semi-circle. The

ept on the horizontal axis is equal to R_0 .

(0(D). The relationship between the im-

y low frequencies, the amplitude of im-

mpedance approaches R_0 . Figure 10(φ = arctanh $\left(\frac{Z'}{Z'}\right) = -\arctanh\left(\frac{R}{R+R_0(1+(\omega\tau))^2}\right)$

Figure 10(B) shows the EIS of the $R_0(R/(C)$ circuit in the Nyquist plot, which is a p

diameter of the semi-circle is equal to R and the high-frequency interce V¹⁶³ T+(ω)² (1)

arotanh $\left[\frac{R\omega}{R+R(d+1(\omega\tau))}\right]$ (2)

arotanh $\left[\frac{R\omega}{R+R(d+1(\omega\tau))}\right]$ (2)

arotanh (EIS of the $R_0(R/(C)$ circuit in the Nyquist plot, which is a perfect semi-circle. The

in-circle is equal to R φ = arctanh $\left(\frac{K}{Z'}\right)$ = -arctanh $\left(\frac{R\omega T}{R\sqrt{M}}\right)$ (79)

Figure 10(B) shows the EIS of the $R_6(Rt/C)$ circuit in the Nyquist plot, which is a perfect semi-circle. The

diameter of the semi-circle is equal to *R* (Z)

Figure 10(B) shows the EIS of the $R_0(R/C)$ circuit in the Nyquist plot, which is a perfect set

diameter of the semi-circle is equal to $R_0(R/C)$ circuit in the Nyquist plot, which is a perfect set

diameter of the s

system,

$$
U_{\rm M} = U_{\rm M}^{\ 0} + \tilde{U}_{\rm M} e^{j\omega^{n l} \tau} \tag{80}
$$

referenced to D/λ_{D}^2 . When the perturbation is sufficiently weak ($\widetilde{\phi}_{M}$ < 25 mV, or \widetilde{U}_{M} < 1), the linear response

$$
C_{+} = C_{+}^{0} + \tilde{C}_{+}e^{j\omega^{n\ell_{\tau}}} \tag{81}
$$

$$
C_{-} = C_{-}^{0} + \widetilde{C}_{-}e^{j\omega^{n d_{\tau}}} \tag{82}
$$

$$
U = U^0 + \widetilde{U}e^{j\omega^{n\ell}\tau} \tag{83}
$$

$$
j\omega^{\text{nd}}\widetilde{C}_{+} = \frac{\partial^{2}\widetilde{C}_{+}}{\partial X^{2}} + \frac{\partial}{\partial X}\left(C_{+}^{0}\frac{\partial\widetilde{U}}{\partial X} + \widetilde{C}_{+}\frac{\partial U^{0}}{\partial X}\right)
$$
\n(84)

angle. The parameters used for calculation are as follows,
$$
h_0 = A - 1
$$
 i.e. $C = 0.5$ r; and the frequency range: 1 × 10⁻¹ h2. to 1 × 10⁻¹ Hz. Matlab script of this model is provided in the supporting information. (color on line)
\nSubstituting Eqs. (81)-(83) into the PNP equation, and omitting the stationary and high-order parts, we obtain,
\n $j\omega^{10}\tilde{C}_x = \frac{\partial^2 \tilde{C}_x}{\partial X^2} + \frac{\partial}{\partial X} \left(C_x \frac{\partial \tilde{U}}{\partial X} + \tilde{C}_x \frac{\partial U^0}{\partial X} \right)$ (84)
\n $j\omega^{10}\tilde{C}_x = \frac{\partial^2 \tilde{C}_x}{\partial X^2} - \frac{\partial}{\partial X} \left(C_x \frac{\partial \tilde{U}}{\partial X} + \tilde{C}_x \frac{\partial U^0}{\partial X} \right)$ (85)
\nUsually, C_y , C_y and U^0 are X-varying, making it difficult to solve Eqs. (84)-(86) analytically. Nevertheless,
\nat the pzc, we have, $C_x^0 = C_y^0 = 1$ and $U^0 = 0$. Therefore, Eqs. (84) and (85) are reduced to,
\n $j\omega^{10} \tilde{C}_x = \frac{\partial^2 \tilde{C}_x}{\partial X^2} + \frac{\partial^2 \tilde{U}}{\partial X^2}$ (87)
\n $j\omega^{10} \tilde{C}_x = \frac{\partial^2 \tilde{C}_x}{\partial X^2} - \frac{\partial^2 \tilde{U}}{\partial X^2}$ (88)
\nSubstituting Eq. (86) into Eqs (87) and (88) leads,
\n $\frac{\partial^2 \tilde{C}_x}{\partial X^2} = -\frac{1}{2} \tilde{C}_x + (j\omega^{10} + \frac{1}{2}) \tilde{C}_x - \frac{1}{2} \tilde{C}_x$ (89)
\nTwo equations above can be rewritten into a matrix form,
\n $\frac{\partial^2 \tilde{C}_x}{\partial X^2} = \mathbf{A x}$ (91)
\n(92)

$$
\frac{\partial^2 \widetilde{U}}{\partial X^2} = \frac{1}{2} (\widetilde{C}_- - \widetilde{C}_+). \tag{86}
$$

Usually, C_{+}^{0} , C_{-}^{0} and U^{0} are X-varying, making it difficult to solve Eqs. at the pzc, we have, $C_+^0 = C_-^0 = 1$ and $U^0 = 0$. Therefore, Eqs. (84) and (85) are reduced to,

$$
j\omega^{\text{nd}}\,\widetilde{C}_{+}=\frac{\partial^{2}\widetilde{C}_{+}}{\partial X^{2}}+\frac{\partial^{2}\widetilde{U}}{\partial X^{2}}
$$
\n(87)

$$
j\omega^{\text{nd}}\,\widetilde{C}_-=\frac{\partial^2\widetilde{C}_-}{\partial X^2}-\frac{\partial^2\widetilde{U}}{\partial X^2}\tag{88}
$$

$$
\frac{\partial^2 \tilde{C}_+}{\partial X^2} = (j\omega^{\text{nd}} + \frac{1}{2})\tilde{C}_+ - \frac{1}{2}\tilde{C}_-\tag{89}
$$

$$
\frac{\partial^2 \widetilde{C}_-}{\partial X^2} = -\frac{1}{2}\widetilde{C}_+ + (j\omega^{\text{nd}} + \frac{1}{2})\widetilde{C}_-\tag{90}
$$

$$
\frac{\partial^2}{\partial X^2} \mathbf{x} = \mathbf{A} \mathbf{x} \tag{91}
$$

Usually,
$$
C_*^{\alpha}
$$
, C_*^{α} and U^{α} are X-varying, making it difficult to solve Eqs. (84)-(86) analytically. Nevertheless,
at the pzc, we have, $C_*^{\alpha} = C_*^{\alpha} = 1$ and $U^{\alpha} = 0$. Therefore, Eqs. (84) and (85) are reduced to,
 $j\omega^{\text{nd}}\tilde{C}_x = \frac{\partial^2 \tilde{C}_x}{\partial X^2} + \frac{\partial^2 \tilde{U}}{\partial X^2}$ (87)
Substituting Eq. (86) into Eqs (87) and (88) leads,
 $\frac{\partial^2 \tilde{C}_x}{\partial X^2} = (j\omega^{\text{nd}} + \frac{1}{2})\tilde{C}_x - \frac{1}{2}\tilde{C}_x$ (89)
 $\frac{\partial^2 \tilde{C}_z}{\partial X^2} = -\frac{1}{2}\tilde{C}_x + (j\omega^{\text{nd}} + \frac{1}{2})\tilde{C}_x$ (90)
Two equations above can be rewritten into a matrix form,
 $\frac{\partial^2}{\partial X^2} \mathbf{x} = \mathbf{A}\mathbf{x}$ (91)
 $\mathbf{A} = \begin{bmatrix} \Theta_1 & \Theta_2 \\ \Theta_2 & \Theta_1 \end{bmatrix}$ (92)
 $\mathbf{x} = [\tilde{C}_+, \tilde{C}_x]^T$ (93)

$$
\mathbf{x} = [\widetilde{C}_+, \widetilde{C}_-]^T
$$
 (93)

$$
\mathbf{\mathcal{H}}E\ddot{\mathbf{\mathcal{H}}}(J. Electrochem.) 2022, 28(2), 2108471 (21 of 30)
$$
\n
$$
\Theta_1 = (j\omega^{nd} + \frac{1}{2})
$$
\n
$$
\Theta_2 = -\frac{1}{2}.
$$
\n(95)\n\nThe eigenvalues, λ_1 and λ_2 , and eigenvectors, V_1 and V_2 , of matrix **A** are,\n
$$
\lambda_1 = \Theta_1 - \Theta_2
$$
\n
$$
\lambda_2 = \Theta_1 + \Theta_2
$$
\n
$$
\lambda_3 = \Theta_1 + \Theta_2
$$
\n(96)\n
$$
\lambda_2 = [1, 1]^T.
$$
\n(97)\n
$$
V_1 = [1, 1]^T.
$$
\n
$$
\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \\ 1 & 1 \end{bmatrix}
$$
\n
$$
\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}
$$
\n
$$
\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}
$$
\n
$$
\mathbf{y} = \mathbf{P}^{-1}\mathbf{x}
$$
\n(102)\n
$$
\mathbf{y} = \mathbf{F}^{-1}\mathbf{x}
$$
\n(103)\nNotice that **H** is a diagonal matrix, implying that the two elements of vector **y**, y_1 and y_2 , can be solved separately,\n
$$
y_1 = \alpha_1 \sinh(\sqrt{\lambda_1} X) + \alpha_2 \cosh(\sqrt{\lambda_1} X)
$$
\n(104)

$$
\Theta_2 = -\frac{1}{2}.
$$
\n(95)
\nThe eigenvalues, λ_1 and λ_2 and eigenvectors, V_1 and V_2 of matrix **A** are,
\n $\lambda_1 = \Theta_1 - \Theta_2$ \n(96)
\n $\lambda_2 = \Theta_1 + \Theta_2$ \n(97)
\n $V_1 = [-1,1]^T$ \n(98)
\nIntroducing two matrices **P** and **H**, and a vector **y**,
\n
$$
\mathbf{P} = \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix}
$$
\n(100)
\n
$$
\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}
$$
\n(101)
\n
$$
\mathbf{y} = \mathbf{P}^{-1}\mathbf{x}
$$
\n(102)
\n
$$
\mathbf{y} = \mathbf{P}^{-1}\mathbf{x}
$$
\n(103)
\nNotice that **H** is a diagonal matrix, implying that the two elements of vector **y**, y_1 and y_2 , can be solved separately,
\nseparately,
\n $y_1 = \alpha_1 \sinh(\sqrt{\lambda_1} X) + \alpha_2 \cosh(\sqrt{\lambda_1} X)$ \n(104)
\n $y_2 = \beta_1 \sinh(\sqrt{\lambda_2} X) + \beta_2 \cosh(\sqrt{\lambda_2} X)$ \n(105)
\nwhere coefficients $\alpha_1, \alpha_2, \beta_1, \beta_2$ are to be determined by the corresponding boundary conditions. Afterwards, the two elements of the vector **x** are obtained as,

$$
V_1 = \begin{bmatrix} -1,1 \end{bmatrix}^T \tag{98}
$$

$$
V_2 = [1,1]^T. \tag{99}
$$

$$
\mathbf{P} = \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix} \tag{100}
$$

$$
\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix} \tag{101}
$$

$$
\mathbf{y} = \mathbf{P}^{-1}\mathbf{x} \tag{102}
$$

$$
\frac{\partial^2}{\partial X^2} \mathbf{y} = \mathbf{H} \mathbf{y}.\tag{103}
$$

separately,

$$
y_1 = \alpha_1 \sinh(\sqrt{\lambda_1} X) + \alpha_2 \cosh(\sqrt{\lambda_1} X) \tag{104}
$$

$$
y_2 = \beta_1 \sinh(\sqrt{\lambda_2} X) + \beta_2 \cosh(\sqrt{\lambda_2} X) \tag{105}
$$

P and **H**, and a vector **y**, V_1 and V_2 , of matrix **A** are, (96)
 P and **H**, and a vector **y**, (100)
 P and **H**, and a vector **y**, (100)

(101)

tor **x** with **y** and using the equality, $P^{\perp}AP = H$, transformin $\lambda_1 = \Theta_1 - \Theta_2$
 $\lambda_2 = \Theta_1 + \Theta_2$
 $V_1 = [-1,1]^T$
 $V_2 = [1,1]^T$.

Introducing two matrixes **P** and **H**, and a vector **y**,
 $\mathbf{P} = \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix}$
 $\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}$
 $\mathbf{y} = \mathbf{P}^{-1}\mathbf{x}$

the (96)

(97)

(97)

(99)

(99)

(100)

(101)

(100)

(101)

(103)

(103)

gonal matrix, implying that the two elements of vector **y**, *y*₁ and *y*₂ can be solved

(03)
 $\cosh(\sqrt{\lambda_1}X)$

(104)
 $\cosh(\sqrt{\lambda_2}X)$

(105)
 $\beta_$ $W_2 = [1,1]^2$
 $V_1 = [-1,1]^2$ (99)
 $W_2 = [1,1]^2$ (100)
 $\mathbf{H} = \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix}$ (100)
 $\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}$ (102)
 $\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \\ 1 & 1 \end{bmatrix}$ (102)
 $\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \\ 1 & 1 \end{bmatrix}$ (102)
 $V_1 = [-1,1]^r$.
 $V_2 = [1,1]^r$.
 $\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_1 \end{bmatrix}$
 $\mathbf{H} = \begin{bmatrix} 1 & 1 \\ 0 & \lambda_1 \end{bmatrix}$.
 $\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_1 \end{bmatrix}$
 $\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_1 \end{bmatrix}$.
 $\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_1 \end{bmatrix}$.

$$
\tilde{C}_+ = -y_1 + y_2 \tag{106}
$$

$$
\widetilde{C}_- = y_1 + y_2. \tag{107}
$$

 $\mathbf{P} = \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix}$ (100)
 $\mathbf{F} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}$ (101)
 $\mathbf{y} = \mathbf{P}^2\mathbf{x}$ (102)
 $\mathbf{y} = \mathbf{P}^3\mathbf{x}$ (102)
 $\frac{\partial^2}{\partial x^2} \mathbf{y} = \mathbf{H}\mathbf{y}.$ (102)
 $\frac{\partial^2}{\partial x^2} \mathbf{y} = \mathbf{H}\mathbf{y}.$ (1 $\mathbf{r} = \begin{bmatrix} 1 & 1 \ 1 & 0 \end{bmatrix}$
 $\mathbf{H} = \begin{bmatrix} \lambda_1 & 0 \ 0 & \lambda_2 \end{bmatrix}$ (101)
 $\mathbf{y} = \mathbf{P}^2 \mathbf{x}$ (102)

then we substitute the vector **x** with **y** and using the equality, $\mathbf{P}^2 \mathbf{A} \mathbf{P} = \mathbf{H}$, transforming Eq **H** = $\begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}$ (101)
 y = **P**ⁱ**x c** ubstitute the vector **x** with **y** and using the equality, **P**¹**AP** = **H**, transforming Eq. (91) into, $\frac{\partial^2}{\partial A^2}$ **y** = **Hy.** (102)

Rotice that **H** is **c** = [0 λ_1] (101)
 c = P^{-x}**x** (102)
 $\hat{\theta}^2 = P^{-1}$ **x** (102)
 $\hat{\theta}^2 = \hat{\theta}^2$ = PFy. (103)
 $\hat{\theta}^2 = \hat{\theta}^2$ = PFy. (103)

SN² = **y** = FFy. (103)

SN² = **P** = PF. (103)

SN² = Concentration, implying tha $y = P^2 x$ (102)

then we substitute the vector **x** with **y** and using the equality, $P^2AP = H$, transforming Eq. (91) into,

(103)
 $\frac{\partial^2}{\partial X^2} y = Hy.$ (103)

Notice that **H** is a diagonal matrix, implying that the two elem then we substitute the vector **x** with **y** and using the equality, $\mathbf{P}^A \mathbf{AP} = \mathbf{H}$, transforming Eq. (91) into,
 $\frac{\partial^2}{\partial x^2}$ **y** = **Hy**. (103)

Notice that **H** is a diagonal matrix, implying that the two eleme $\sqrt{A_1}X$ + α , cosh($\sqrt{A_2}X$) (104)

(104)

(105)

cients α , α , β , β , are to be determined by the corresponding boundary conditions. Afterwards, the two

the vector **x** are obtained as, (106)

exector **x** where coefficients a_k , a_k , β_1 , β_2 are to be determined by the corresponding boundary conditions. Afterwards, the two

clements of the vector **x** are obtained as,
 \vec{c} . \vec{e} -y₁ + y₂ (106)
 \vec{c} . ons of Eqs. (106) and (107) are as follows. In the bulk solution, $X = X_{1n}$ the clectric potential
rence, namely, it does not change with the excitation. In addition, all ions have their bulk
also do not change with the p The boundary conditions of Fqs. (106) and (107) are as follows. In the bulk solution, $X = X_n$, the electric potential

is regarded as the reference, namely, it does not change with the excitation. In addition, all ions hav

$$
\widetilde{C}_+ = 0, \ \widetilde{C}_- = 0, \ \widetilde{U} = 0. \tag{108}
$$

$$
\frac{\partial \widetilde{C}_{+}}{\partial X} + \frac{\partial \widetilde{U}}{\partial X} = -\frac{\lambda_{\rm D} \widetilde{J}_{\rm de}}{D c_0} \tag{109}
$$

$$
\frac{\partial \widetilde{C}_{-}}{\partial X} - \frac{\partial \widetilde{U}}{\partial X} = 0
$$
\n(110)

$$
\widetilde{U}_{\text{HP}} = \widetilde{U}_{\text{M}} + \frac{\epsilon \delta_{\text{HP}}}{\epsilon_{\text{HP}} \lambda_{\text{D}}} \frac{\partial \widetilde{U}}{\partial X}
$$
\n(111)

$$
\frac{F\eta}{RT} = \Pi, \ \Pi = \Pi^0 + \widetilde{\Pi} \tag{112}
$$

where $\Pi^0 = U_M^0 - U_{HP}^0 - U_{eq}$ is the dimensionless stationary overpotential and $\Pi =$

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netal ions deposition, M⁺ + e⁻ ↔ M, occurring at the HP. The current density of the

FBV equation,
 $\left(-\frac{(1-\alpha)e_0\eta}{k_B T}\right)$ (113)

$$
\frac{d_2E}{d_2E} = \frac{1}{2} \left(\frac{E}{E} \left(\frac{E}{E} \left(\frac{E}{E} \right) \right) \left(\frac{1}{2} \right
$$

where $c_{\text{+HP}}$ is the concentration of M⁺ at the HP, c_{+}^{0} is the concentrations of M⁺ in the bulk solution, and k_0 is the

$$
j_{\alpha} = k_0 \left[\exp(\alpha (\Pi^0 + \widetilde{\Pi})) - (C_+^0 + \widetilde{C}_+) \exp(-(1-\alpha)(\Pi^0 + \widetilde{\Pi})) \right]
$$
(114)

$$
j_{\text{de}} = k_0 [\exp(\alpha \Pi^0)(1 + \alpha \widetilde{\Pi}) - (C_+^0 + \widetilde{C}_+) \exp(-(1 - \alpha)\Pi^0)(1 - (1 - \alpha)\widetilde{\Pi})]
$$
\nPomoving the stationary part and second order parts, we obtain

$$
\tilde{J}_{\text{de}} = k_0 \left[(\alpha \exp(\alpha \Pi^0) + (1 - \alpha) C_+{}^0 \exp(-(1 - \alpha) \Pi^0) \widetilde{\Pi} - \exp(-(1 - \alpha) \Pi^0) \widetilde{C}_+ \right].
$$
\n(116)

$$
\nu_1 = k_0(\alpha \exp(\alpha \Pi^0) + (1-\alpha)C_+^0 \exp(-(1-\alpha)\Pi^0)), \quad \nu_2 = k_0 \exp(-(1-\alpha)\Pi^0)
$$
\nWe can reformulate Eq. (116) as

$$
\tilde{J}_{\text{de}} = \nu_1 (\tilde{U}_{\text{M}} - \tilde{U}_{\text{HP}}) - \nu_2 \tilde{C}_+ \,. \tag{11}
$$

$$
i_{\omega} = k_{0} \left(\exp\left(\frac{\pi e_{\theta} \eta}{k_{B}T}\right) - \frac{c_{\theta} \eta e}{r_{B}T} \exp\left(-\frac{(1 - \alpha)e_{\theta} \eta}{r_{B}T}\right)\right)
$$
\n(113)
\nwhere e_{θ} is the concentration of M⁺ at the HP, e^{+} is the concentrations of M⁺ in the bulk solution, and k_{S} is the
\nreaction rate constant.
\nSubstituting Eq. (81) and (112) into the FBV theory, Eq. (113), gives,
\n
$$
k_{B} = k_{\omega}[\exp(\alpha[\Gamma^{0}(1 + \alpha \overline{1})) - (C^{+} + \overline{C}) \exp(-(-1 - \alpha)[\Gamma^{0}(1 - (-\alpha)\overline{1}\overline{1})]
$$
\n(114)
\nExpanding Eq. (114) into a first-order Taylor series leads to,
\n $j_{\omega} = k_{\omega}[\exp(\alpha[\Gamma^{0}(1 + \alpha \overline{1})) - (C^{+} + \overline{C}) \exp(-(-1 - \alpha)[\Gamma^{0}(1 - (-\alpha)\overline{1}\overline{1})]$
\nHermoving the stationary parts and second-order parts, we obtain,
\n $\nu_{\alpha} = k_{\alpha}[\exp(\alpha[\Gamma^{0}(1 + \alpha \overline{1} \overline{1}) - C^{+} \exp(-(-1 - \alpha)\overline{1}\overline{1})]$
\n $\nu_{\alpha} = \pi_{\alpha}[\cos(\alpha[\Gamma^{0}(1 + \alpha \overline{1}) - C^{+} \exp(-(-1 - \alpha)\overline{1}\overline{1})]$, $\nu_{\beta} = k_{\alpha} \exp(-(-1 - \alpha)\overline{1}\overline{1})$
\n $\nu_{\alpha} = k_{\alpha}(\cos(\alpha[\Gamma^{0}(1 + \alpha \overline{1}) - C^{+} \exp(-(-1 - \alpha)\overline{1}\overline{1})]$, $\nu_{\beta} = k_{\alpha} \exp(-(-1 - \alpha)\overline{1}\overline{1})$
\n $\bar{L}_{\alpha} = \nu_{\alpha}(\overline{L}_{\alpha} - \overline{L}_{\alpha}) = \nu_{\alpha} \bar{L}_{\alpha}.$
\nS.1.4 Implementing Fig. (106),
\n $\sigma_{\$

$$
\alpha_2 = -\alpha_1 \tanh(\sqrt{\lambda_1} X_b) \tag{120}
$$

$$
\beta_1 = -\frac{1}{\sqrt{\lambda_2}} \left[\alpha_1 \left(\sqrt{\lambda_1} - \frac{1}{\sqrt{\lambda_1}} + \frac{1}{r_c + X_b} \left(\frac{r_c}{\sqrt{\lambda_1}} + \frac{\tanh(\sqrt{\lambda_1} X_b)}{\lambda_1} \right) \right) + \frac{1}{r_c + X_b} \widetilde{U}_M \right]
$$
(121)

$$
\beta_2 = \frac{1}{\sqrt{\lambda_2}} \left(\alpha_1 \left(\sqrt{\lambda_1} - \frac{1}{\sqrt{\lambda_1}} + \frac{1}{r_c + X_b} \left(\frac{r_c}{\sqrt{\lambda_1}} + \frac{\tanh(\sqrt{\lambda_1} X_b)}{\lambda_1} \right) \right) + \frac{1}{r_c + X_b} \widetilde{U}_M \right) \tanh(\sqrt{\lambda_2} X_b)
$$
(122)

$$
\left|\frac{\tan \left(\sqrt{\lambda_1} \, t_k\right) \left(\lambda_1 \, r_c + X_b - 2\right)}{2\sqrt{\lambda_2}} \right| r_c + X_b \sqrt{\lambda_1}
$$
\n
$$
\alpha_2 = -\alpha_1 \tanh(\sqrt{\lambda_1} \, X_b)
$$
\n
$$
\beta_1 = -\frac{1}{\sqrt{\lambda_2}} \left(\alpha_1 \left(\sqrt{\lambda_1} - \frac{1}{\sqrt{\lambda_1}} + \frac{1}{r_c + X_b} \left(\frac{r_c}{\sqrt{\lambda_1}} + \frac{\tanh(\sqrt{\lambda_1} X_b)}{\lambda_1} \right) \right) + \frac{1}{r_c + X_b} \tilde{U}_M \right)
$$
\n
$$
\beta_2 = \frac{1}{\sqrt{\lambda_2}} \left(\alpha_1 \left(\sqrt{\lambda_1} - \frac{1}{\sqrt{\lambda_1}} + \frac{1}{r_c + X_b} \left(\frac{r_c}{\sqrt{\lambda_1}} + \frac{\tanh(\sqrt{\lambda_1} X_b)}{\lambda_1} \right) \right) + \frac{1}{r_c + X_b} \tilde{U}_M \right) \tanh(\sqrt{\lambda_2} X_b)
$$
\n
$$
\text{where } r_c = \frac{\epsilon_s \delta_{\text{HP}}}{\epsilon_{\text{HP}} \lambda_0} \text{ is the ratio between the Gouy-Chapman capacitance } \left(C_{\text{GC}} - \frac{\epsilon_s}{\lambda_0} \right) \text{ and the Helmholtz capacitor}
$$
\n
$$
\text{ance } \left(C_{\text{H}} = \frac{\epsilon_{\text{HP}}}{\delta_{\text{HP}}} \right).
$$
\n
$$
\text{Then we obtain the explicit expression of } \tilde{J}_\text{dc} \text{ expressed in Eq. (118) by substituting Eqs. (119)-(122) into Eqs.}
$$
\n
$$
(104) \text{ and } (107). \text{ Besides the reaction current density } j_\text{dc}, \text{ the EDL current density also needs to be calculated, expressed as,}
$$
\n
$$
j_\text{d} = -\frac{dq_a}{dt} = -\frac{d(F \int_0^{k} (c_x - c) dx)}{dt}
$$
\n
$$
\text{where } q_a \text{ is the total charges stored in EDL. The dimensionless form of } j_a \text{ is,}
$$
\n
$$
(123)
$$

$$
j_{\rm dl} = -\frac{\mathrm{d}q_{\rm dl}}{\mathrm{d}t} = -\frac{\mathrm{d}(F\int_{0}^{x_{\rm b}}(c_{+} - c_{-})\mathrm{d}x)}{\mathrm{d}t}
$$
(123)

$$
\mathbb{E} \{E \neq (J \ \text{Electrochem.}) 2022, 28(2), 2108471 (23 of 30)
$$
\n
$$
J_{\mathfrak{m}} = -\frac{\mathsf{d} \left(\int_{0}^{x_{k}} (C_{+} - C_{-}) \mathsf{d}X \right)}{\mathsf{d}\tau}
$$
\nConverting Eq. (124) into frequency domain gives,
\n
$$
\tilde{J}_{\mathfrak{m}} = -j\omega^{\text{nd}} \int_{0}^{x_{k}} (\tilde{C}_{+} - \tilde{C}_{-}) \mathsf{d}X.
$$
\n(125)
\nThe total current density is the sum of the double layer current density and the Faradic reaction current density, namely,
\n
$$
\tilde{J} = \tilde{J}_{\mathfrak{m}} + \frac{\lambda_{\text{D}}}{D c_{0}} \tilde{J}_{\mathfrak{a}}.
$$
\n(126)
\nSo far, we obtain the dimensionless impedance expression,
\n
$$
\mathbb{Z}^{\text{nd}} = \frac{\tilde{U}_{\mathfrak{m}}}{\sqrt{\lambda_{1}}} = \frac{r_{\epsilon} \lambda_{1} + X_{\text{b}} (\lambda_{1} - 1) + \frac{\tanh(\sqrt{\lambda_{1}} X_{\text{b}})}{\sqrt{\lambda_{1}}} + \sum_{\mathfrak{a}}^{1}
$$
\n(127)

$$
\tilde{J}_{\rm dl} = -j\omega^{\rm nd} \int_0^{X_b} (\tilde{C}_+ - \tilde{C}_-) \mathrm{d}X. \tag{125}
$$

$$
\tilde{J} = \tilde{J}_{\rm dl} + \frac{\lambda_{\rm D}}{Dc_0} \tilde{J}_{\rm de}.
$$
\n(126)

$$
\frac{\text{d} \ell \# \mathcal{L} \# (J. Electrochem.) 2022, 28(2), 2108471 (23 of 30)}
$$
\n
$$
J_{\text{d}} = -\frac{\text{d} \left(\int_{0}^{x_{\text{L}}} (C_{\text{L}} - C_{\text{L}}) \text{d}X \right)}{\text{d}\tau}
$$
\n(124)\nConverting Eq. (124) into frequency domain gives,
\n
$$
\bar{J}_{\text{d}} = -j\omega^{\text{nd}} \int_{0}^{x_{\text{L}}} (\tilde{C}_{\text{L}} - \tilde{C}_{\text{L}}) \text{d}X.
$$
\n(125)\n\nThe total current density is the sum of the double layer current density and the Faradic reaction current density, namely,
\n
$$
\tilde{J} = \tilde{J}_{\text{d}} + \frac{\lambda_{\text{D}}}{D_{\text{c}}}, \tilde{J}_{\text{d}}.
$$
\n(126)\n\nSo far, we obtain the dimensionless impedance expression,
\n
$$
Z^{\text{nd}} = \frac{\tilde{U}_{\text{M}}}{\tilde{J}} = \frac{r_{\text{c}} \lambda_{1} + X_{\text{b}} (\lambda_{1} - 1) + \frac{\tanh(\sqrt{\lambda_{1}} X_{\text{b}})}{\sqrt{\lambda_{1}}} + \Sigma_{\text{d}} \frac{1}{\lambda_{\text{d}}}
$$
\n(127)\n\nwhere Σ_{d}^{+} and Σ_{d}^{2} represent the terms related to the coupling of charge transfer reaction and ion transport,
\n
$$
\Sigma_{\text{d}}^{1} = -\frac{1}{2} \frac{\lambda_{\text{D}}}{D_{\text{c}}} r_{\text{c}} \nu_{1} \left(\frac{\tanh(\sqrt{\lambda_{1}} X_{\text{b}})}{\sqrt{\lambda_{1}}} - X_{\text{b}} \right) +
$$

where \sum_{d}^{1} and \sum_{d}^{2} represent the terms related to the coupling of charge transfer reaction and

4.
$$
\frac{d}{dr} \left(\int_{0}^{R} (C_{\tau} - C_{\tau}) dX \right)
$$

\n $J_{\mu} = -\frac{d}{dr} \left(\int_{0}^{R} (C_{\tau} - C_{\tau}) dX \right)$
\n $J_{\mu} = -\frac{d}{dr} \left(\int_{0}^{R} (1/24) \text{ into frequency domain gives,}$
\n $J_{\mu} = -j\omega^{-1} \int_{0}^{R} (\tilde{C}_{\tau} - \tilde{C}_{\tau}) dX.$
\n(125)
\nThe total current density is the sum of the double layer current density and the Faradic reaction current
\ndensity; namely,
\n $\tilde{J} = \tilde{J}_{\mu} + \frac{\lambda_{\text{B}}}{D_{\text{C}_0}} \tilde{J}_{\mu}.$
\nSo far, we obtain the dimensionless impedance expression,
\n
$$
\chi^{\mu} = \frac{\tilde{U}_{\mu}}{\tilde{J}} = \frac{r_{\xi} \lambda_{1} + X_{\xi} (\lambda_{1} - 1) + \frac{\tanh(\sqrt{\lambda_{1}} X_{\text{b}})}{\sqrt{\lambda_{1}}} + \Sigma_{\alpha}^{\perp}
$$

\nwhere Σ_{ω}^{\perp} and Σ_{ω}^{\perp} represent the terms related to the coupling of charge transfer reaction and ion transport,
\n
$$
\Sigma_{\omega}^{\perp} = -\frac{1}{2} \frac{\lambda_{\text{B}}}{D_{\text{C}_0}} r_{\epsilon} p_{\epsilon} \left(\frac{\tanh(\sqrt{\lambda_{1} X_{\text{b}}})}{\sqrt{\lambda_{1}}} - X_{\text{b}} \right) + \frac{1}{2} \frac{\tanh(\sqrt{\lambda_{1} X_{\text{b}}})}{\sqrt{\lambda_{2}}} + (r_{\epsilon} + X_{\text{a}}) \sqrt{\lambda_{1}} \tanh(\sqrt{\lambda_{1} X_{\text{b}}})
$$
(128)
\n
$$
\Sigma_{\omega}^{\perp} = \frac{\lambda_{\text{B}}}{D_{\text{C}_0}} r_{\epsilon} p_{\epsilon} \left(\frac{\tanh(\sqrt{\lambda_{1} X_{\text{b}}})}{\sqrt{\lambda_{1}}} - r_{\epsilon} p_{\epsilon} \lambda_{2}) (1 - \text{sech}(\sqrt{\lambda_{1} X_{\text{b}}}) + r_{\epsilon} r_{\epsilon} \lambda_{1})
$$

$$
\Sigma_{\rm dr}^2 = \frac{\lambda_{\rm D}}{Dc_0} \left(\sqrt{\lambda_2} v_2 \tanh(\sqrt{\lambda_2} X_{\rm b}) - v_1 r_{\rm c} \lambda_2 \right) (1 - \text{sech}(\sqrt{\lambda_1} X_{\rm b})) + v_1 r_{\rm c} \lambda_1 \frac{\lambda_{\rm D}}{Dc_0} + \frac{\lambda_{\rm D}}{Dc_0} v_2 \sqrt{\lambda_1} \tanh(\sqrt{\lambda_1} X_{\rm b}) \tag{129}
$$

2

 $2\lambda_D^2$ DC_{GC} $\frac{1}{dt}$ = \sum_{dr}^{2} = 0, and Eq. (127) is reduced to the

 r_c , then we obtain,

$$
2\omega_{\alpha} = -\frac{1}{2} \frac{\lambda_{\rm D}}{Dc_{\rm o}} r_{\rm c} v_{\rm l} \left| \frac{\lambda_{\rm A}}{\sqrt{\lambda_{\rm I}}} - \lambda_{\rm b} \right| + \frac{1}{2} \frac{\lambda_{\rm D}}{Dc_{\rm o}} v_{\rm 2} \left| \left[r_{\rm c} \lambda_{\rm I} + X_{\rm s} (\lambda_{\rm I} - 1) + \frac{\tanh(\sqrt{\lambda_{\rm I}} \, X_{\rm b})}{\sqrt{\lambda_{\rm I}}} \right] \frac{\tanh(\sqrt{\lambda_{\rm I}} \, X_{\rm b}) + v_{\rm r} \lambda_{\rm A} \lambda_{\rm B} \sqrt{\lambda_{\rm I}} \tanh(\sqrt{\lambda_{\rm I}} \, X_{\rm b}) \right] \qquad (128)
$$
\n
$$
\sum_{\alpha}^{2} = \frac{\lambda_{\rm D}}{Dc_{\rm o}} (\sqrt{\lambda_{\rm I}} v_{\rm I} \tanh(\sqrt{\lambda_{\rm I}} \, X_{\rm b}) - v_{\rm r} r_{\rm A} \lambda_{\rm J} (1 - \text{sech}(\sqrt{\lambda_{\rm I}} \, X_{\rm b}) + v_{\rm r} r_{\rm A} \lambda_{\rm D} \frac{\lambda_{\rm D}}{Dc_{\rm o}} + \frac{\lambda_{\rm D}}{Dc_{\rm o}} v_{\rm J} \sqrt{\lambda_{\rm I}} \tanh(\sqrt{\lambda_{\rm I}} \, X_{\rm b}) \qquad (129)
$$
\nBased on previously defined dimensionless variables, we obtain the impedance reference, $Z_{\rm ref} = \frac{2\lambda_0^2}{DC_{\rm cc}}$.

\nNotably, if there is no reaction at the HP, $v_1 = v_2 = 0$, we obtain $\sum_{\alpha}^{2} = \sum_{\alpha}^{2} = 0$, and Eq. (127) is reduced to the
improddance of an ideal polarizable electron at the PP, $v_1 = v_2 = 0$, we obtain $\sum_{\alpha}^{2} = \sum_{\alpha}^{2} = 0$, and Eq. (127) is reduced to the
divergence of an ideal polarizable electron. The energy, we have $\lambda_{\rm E} \gg 1 \approx$

\nso that, we obtain,

\n
$$
\sum_{\alpha}^{2} \frac{\lambda_{\rm D}}{Dc_{\rm o}} \left| \frac{\lambda
$$

$$
\frac{\Sigma_{dp}^2}{j\omega^{nd}} \approx \frac{\lambda_D}{Dc_0} \left(\frac{v_2 \tanh(\sqrt{j\omega^{nd}} X_b)}{\sqrt{j\omega^{nd}}} - v_1 r_c \right) + v_1 r_c \frac{\lambda_D}{Dc_0} + \frac{v_1 r_c}{j\omega^{nd}} \frac{\lambda_D}{Dc_0} + \frac{\lambda_D}{Dc_0} v_2 \frac{\sqrt{1 + j\omega^{nd}}}{j\omega^{nd}}
$$
(131)

$$
Z^{\rm nd} = \frac{X_{\rm b}}{2} + \frac{\left(\frac{r_{\rm c}}{j\omega^{\rm nd}} + \frac{1}{j\omega^{\rm nd}\sqrt{j\omega^{\rm nd}+1}}\right) + \frac{\lambda_{\rm D}}{Dc_0} \frac{1}{j\omega^{\rm nd}\sqrt{1+j\omega^{\rm nd}}} \left(\frac{v_2}{2} \frac{\tanh(\sqrt{j\omega^{\rm nd}} X_{\rm b})}{\sqrt{j\omega^{\rm nd}}} - \frac{v_1 r_{\rm c}}{2}\right)}{\sqrt{j\omega^{\rm nd}}}
$$
\n
$$
2 + v_2 \frac{\lambda_{\rm D}}{Dc_0} \left(\frac{\tanh(\sqrt{j\omega^{\rm nd}} X_{\rm b})}{\sqrt{j\omega^{\rm nd}}} + \frac{\sqrt{1+j\omega^{\rm nd}}}{j\omega^{\rm nd}}\right) + v_1 r_{\rm c} \frac{\lambda_{\rm D}}{Dc_0} \frac{1}{j\omega^{\rm nd}}
$$
\n(132)

Usually, $\omega^{nd} = \omega \frac{\lambda_D^2}{D} \approx \omega \times 10^{-9} \ll 1$, then we obtain,

$$
Z^{a} = \frac{X_{b}}{2} + \frac{\left(\frac{r_{c}}{j\omega^{ab}} + \frac{1}{j\omega^{ab}\sqrt{j\omega^{b-1}} + 1}\right) + \frac{\lambda_{0}}{j\omega_{0}} - \frac{1}{j\omega^{ab}\sqrt{1 + j\omega^{b-1}}} \left(\frac{v_{2}}{2} \frac{\tanh(\sqrt{j\omega^{a}} \cdot X_{b})}{\sqrt{j\omega^{ab}}} - \frac{v_{1}r_{c}}{2}\right)}{2 + v_{2} \frac{\lambda_{0}}{2} \left(\frac{\tanh(\sqrt{j\omega^{a}} X_{b})}{\sqrt{j\omega^{b-1}} + \sqrt{1 + j\omega^{b-1}}} \right) + v_{1}r_{c} \frac{\lambda_{0}}{2} - \frac{1}{2}} - \frac{1}{2}
$$
\n
$$
= \frac{X_{b}}{2} + \frac{\frac{1 + r_{c}}{j\omega^{ab}} - \frac{\lambda_{0}}{2} \frac{1}{2} \left(\frac{v_{2}}{2} \frac{\tanh(\sqrt{j\omega^{a}} X_{b})}{\sqrt{j\omega^{a}}} + \frac{\sqrt{1 + j\omega^{a-1}}}{2} \right) + v_{1}r_{c} \frac{\lambda_{0}}{2} - \frac{1}{j\omega^{a}} - \frac{1}{j\omega_{0}} - \frac{1}{j\omega_{0}} \frac{v_{1}}{2} \frac{\tanh(\sqrt{j\omega^{a}} X_{b})}{\sqrt{j\omega^{a}}} - \frac{v_{1}r_{c}}{2} \frac{1}{2}
$$
\n
$$
= \frac{X_{b}}{2} + \frac{1}{2} - \frac{\lambda_{0}}{2} - \frac{\lambda_{0}}{2} \frac{\tanh(\sqrt{j\omega^{a}} X_{b})}{\sqrt{j\omega^{a}}} + \frac{1}{2} \frac{\lambda_{0}}{2} \frac{1}{2} \frac{1}{2} \frac{\lambda_{0}}{2} \frac{1}{2} \left(\frac{1}{2} - \frac{\lambda_{0}}{2} \frac{v_{1}r_{c}}{\sqrt{j\omega^{a}}} + \frac{1}{2} \frac{\lambda_{0}}{2} \frac{1}{2} \frac{v_{1}r_{c}}{\sqrt{j\omega^{a}}} + \frac{1}{2} \frac{\lambda_{0}}{2} \frac{v_{1}r_{c}}{\sqrt{j\omega^{a}}} + \frac{1}{2} \frac{\lambda_{0}}{2} \frac{v_{1}r_{c
$$

We notice that the final expression of Eq. (133) has a coefficient of $\frac{1}{2}$, which may look a little weird to readers. 2 DC_{GC} , when Eq. (155) is recommended as,

$$
\frac{A_b}{2} + \frac{1}{2} \underbrace{\frac{j\omega^{nl}}{j\omega^{n+}} + \frac{1}{\frac{2}{v_2} \frac{Dc_0}{A_0} (1 + r_c) - \frac{v_1 r_c}{v_2} + \frac{\tanh(\sqrt{j\omega^{nl}} X_b)}{\sqrt{j\omega^{nl}}} }
$$
\nWe notice that the final expression of Eq. (133) has a coefficient of $\frac{1}{2}$, which may look a little weird to readers.
\nTherefore, we redefine the impedance reference as $\frac{A_D^2}{DC_{CC}}$, then Eq. (133) is reformulated as,
\n
$$
Z^{nl} = X_b + \frac{1}{\frac{j\omega^{nl}}{1 + r_c} + \frac{1}{\frac{2}{v_2} \frac{Dc_0}{A_D} (1 + r_c) - \frac{v_1 r_c}{v_2} + \frac{\tanh(\sqrt{j\omega^{nl} X_b})}{\sqrt{j\omega^{nl}}}}
$$
\nWe define, $R_c^{nl} = X_b$ the dimensionless solution resistance, $R_a^{nl} = \frac{2}{v_2} \frac{Dc_0}{\lambda_D} (1 + r_c) - \frac{v_1 r_c}{v_2}$ the dimensionless charge transfer resistance and $W^{nl} = \frac{\tanh(\sqrt{j\omega^{nl} X_b})}{\sqrt{j\omega^{nl}}}$ the dimensionless Warburg impedance. Eq. (134) embodies the coupling relationship between charge transfer reaction and EDL charging. Specifically, both R_a^{nl} and C_a^{nl} have the capacitance ratio term, r_c .
\nThen Eq. (133) is reformulated as,
\n
$$
T^{nl} = R_s^{nl} + \frac{1}{j\omega^{nl} C_a^{nl} + \frac{1}{R_a^{nl} + W^{nl}}}
$$
\nFrom this simplified condition, we define the characteristic frequency of charge transfer reaction as, $\omega_a^{nl} = \frac{1}{R_s^{nl}}$.
\nWhen $\omega^{nl} \le \omega_a^{nl}$, Eq. (135) is simplified to,
\n
$$
Z^{nl} = R_s^{ml} + \frac{\tanh(\sqrt{j\omega^{nl} X_b})}{\sqrt{j\omega^{nl}}}
$$
\n(136)
\nwhich follows. By equation, we define the characteristic frequency of charge transfer reaction as, $\omega_a^{nl} = \frac{1}{R_s^{nl}}$.
\nWhen $\omega^{nl} \le \omega_a^{nl}$, Eq. (135) is simplified to,
\n<math display="block</math>

 $\frac{2}{v_2} \frac{Dc_0}{\lambda_{\rm D}} (1 + r_{\rm c}) - \frac{v_1 r_{\rm c}}{v_2}$ the dimensionless charge v_2 $\frac{\tanh(\sqrt{j\omega^{nd}}X_b)}{t}$ the dimensionless Warburg impedance Eq. (134) embodies the

 $\sqrt{j}\omega^{nd}$

$$
Znd = Rsnd + \frac{1}{j\omegandCdlnd + \frac{1}{Rctnd + Wnd}}
$$
(135)

 1 and the characteristic frequency $\frac{D}{x_b^2}$, whose dimensionless form is $\omega_d^{\text{nd}} = \frac{1}{X_b^2}$. $X_{\rm b}^2$. $2 \cdot$. We define, $R_x^{\text{xi}} = X_b$, the dimensionless solution resistance, $R_a^{\text{xi}} = \frac{2}{v_2} \frac{Dc_0}{\lambda_0} (1 + r_c) - \frac{v_1 r_c}{v_2}$ the dimension
transfer resistance and $W^{\text{xi}} = \frac{\tanh(\sqrt{j\omega^{\text{xi}}/X_s})}{\sqrt{j\omega^{\text{xi}}}}$ the dimensionless Wa nensionless solution resistance, $R_{\alpha}^{nd} = \frac{2}{v_2} \frac{D c_0}{\lambda_D} (1 + r_c) - \frac{v_1 r_c}{v_2}$ the dimensionless charge
 $= \frac{\tanh(\sqrt{j\omega^{nl}} \chi_b)}{\sqrt{j\omega^{nl}}}$ the dimensionless Warburg impedance. Eq.(134) embodies the

veven charge transfe We define, $R_s^{--} = A_s$ the dimensionless solution resistance, $R_d^{--} = \frac{1}{v_2} \frac{1}{\Lambda_D} (1 + r_c)$ = -

transfer resistance and $W^{sd} = \frac{\tanh(\sqrt{j\omega^{sd}} X_s)}{\sqrt{j\omega^{sd}}}$ the dimensionless Warburg impede

coupling relationships between c

When $\omega^{\text{nd}} < \omega_{\text{d}}^{\text{nd}}$, Eq. (135) is simplified to,

$$
Znd = Rsnd + \frac{\tanh(\sqrt{j\omega^{nd}} X_b)}{\sqrt{j\omega^{nd}}}
$$
 (136)

When $\omega_d^{\text{nd}} < \omega^{\text{nd}} < \omega_{\text{ct}}^{\text{nd}}$, Eq. (136) is reduced to,

$$
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$$
\nWhen $\omega_d^{\text{nd}} < \omega^{\text{nd}} < \omega_{\text{ct}}^{\text{nd}},$ Eq. (136) is reduced to,
\n
$$
Z^{\text{nd}} = R_s^{\text{nd}} + \frac{1}{j\omega^{\text{nd}}C_d^{\text{nd}} + \frac{1}{R_{\text{ct}}^{\text{nd}}}}
$$
\nwhose Nyquist plot is an ideal semi-circle, as shown in Figure 11(C), representing the charge transfer reaction.
\nFinally, when $\omega^{\text{nd}} > \omega_{\text{ct}}^{\text{nd}},$ Eq. (137) is reduced to,
\n
$$
Z^{\text{nd}} = R_s^{\text{nd}} + \frac{1}{j\omega^{\text{nd}}C_d^{\text{nd}}}
$$
\n(138)
\nwhose Nyquist plot is a straight line representing the EDL charging process, as shown in Figure 11(B).
\n5.2 Numerical Methods of Impedance Calculation

$$
Znd = Rsnd + \frac{1}{j\omegandCdlnd}
$$
(138)

When $\omega_n^{(m)} < \omega^{n-1} < \omega_n^{n-1}$

When $\omega_n^{(m)} < \omega^{n-1} < \omega_n^{n-1}$, Eq. (136) is reduced to,
 $Z^{n\bar{n}} = R_n^{n\bar{n}l} + \frac{1}{j\omega^{n-1}C_n^{n-1} + \frac{1}{R_n^{n}}}}$

whose Nyquist plot is an ideal semi-circle, as shown in Figure 11(C), repr $\frac{\text{#}\{E\cong (J. Electrochem.) 2022, 28(2), 2108471\ (25 of 30)}{\text{When } \omega_a^{-1} < \omega_a^{-1}, \text{ Eq. (136) is reduced to,}}$

When $\omega_a^{-1} < \omega_a^{-1}$, Eq. (136) is reduced to,
 $Z^{-4} = R_x^{n+1} + \frac{1}{j\omega^{nC} \omega_a^{-1}} + \frac{1}{R_a^{n+1}}$

whose Nyquist plot is an ideal se $\mathbb{E}R_{\text{c}}^{ud} \leq \omega^{ud} \leq \omega_{\text{a}}^{ud}, \mathbb{E}_0$. (136) is reduced to,

When $\omega_n^{ud} \leq \omega^{ud} \leq \omega_n^{ud}$, Eq. (136) is reduced to,
 $Z^{\text{d}} = R_1^{ud} + \frac{1}{j\omega^{ud}C_a^{ud} + \frac{1}{R_a^{ud}}}$ (137)

loose Nyquist plot is an ideal semi-eiri the $\frac{d\theta}{dt} \propto \omega^{n/2}$, $\omega^{n/2}$, $\omega^{n/2$. Then $\omega_s^{rel} \leq \omega_l^{rel} \leq \omega_{\text{tr}}^{rel}$, Fq. (136) is reduced to,
 $Z^{\text{si}} = R_s^{\text{si}} + \frac{1}{j\omega_l^{rel}C_d^{rel}} + \frac{1}{R_s\omega^{rel}}$ (137)

whose Nyquist plot is an ideal semi-circle, as shown in Figure 11(C), representing the charge tran **ts** $\{E\}^{\infty}(L \text{ *Electrochem*) } 2022, 28(2), 2108471 (25 \text{ of } 30)$

When $\omega_A^{m/2} \propto \omega_B^{m/2}$, Eq. (136) is reduced to,
 $Z^{\infty} = R^{-\infty} + \frac{1}{R^{-\infty}}$ (136)

whose Nyquist plot is an ideal semi-circle, as shown in Figure 11(C $\frac{4}{3}(k\frac{\omega_2}{l^2}C_L \text{ *Electronen*}) 2022, 28(2), 2108471 (25 of 30)
\nWhen $\omega_n^{\text{ad}} < \omega_n^{\text{ad}} < \omega_n^{\text{ad}}$, Eq. (136) is reduced to,
\n
$$
Z^{\text{st}} = R_n^{\text{ad}} + \frac{1}{j\omega^{\text{ad}}C_n^{\text{at}}} + \frac{1}{R_n^{\text{ad}}}
$$
\nwhose Nyquist plot is an ideal semi-circle, as shown in Figure 11(C), representing the charge transfer
\nFinally, when $\omega^{\text{ad}} > \omega_n$$ When $\omega_n^{1d} < \omega^{n/d} < \omega_n^{n/d}$, Eq. (136) is reduced to,
 $Z^n = R_n^{n/d} + \frac{1}{j\omega^{n/d}c_n^{n/d}} + \frac{1}{R_n^{n/d}}$ (137)

nose Nyquist plot is an ideal semi-circle, as shown in Figure 11(C), representing the charge transfer reaction.

F When $\omega_d \propto \omega^{-2} \propto \omega_{\alpha}^{-2}$, Eq. (150) is reduced to,
 $Z^{\text{nt}} = R_{\epsilon}^{\text{nt}} + \frac{1}{j\omega^{\alpha} C_{\alpha}^{\text{nt}} + \frac{1}{R_{\epsilon}^{\text{nt}}}}$

whose Nyquist plot is an ideal semi-circle, as shown in Figure 11(C), representing

Finally, when whose Nyquist plot is an ideal semi-circle, as shown in Figure 11(C), representing the charge transfer reaction.

Finally, when $\omega^{n+} > \omega_n^{-d}$, Eq. (137) is reduced to,
 $Z^n = R_n^{-d} + \frac{1}{j\omega^n C_n^{-d}}$ (138)

whose Nyquist plo Finally, when $\omega^{nl} > \omega_{\alpha}^{-il}$. Eq. (137) is reduced to,
 $Z^{nl} = R_s^{ml} + \frac{1}{j\omega^{nl}C_d^{ml}}$

whose Nyquist plot is a straight line representing the EDL charging process, as shown in Fi
 $Z^{nl} = R_s^{ml} + \frac{1}{j\omega^{nl}C_d^{ml}}$

In this

$$
\hat{h}(t) = \left(\sigma(t) - \sigma\left(t - \sum_{i=1}^{1} \Delta t_i\right)\right) \cdot \left(h_1 + \frac{h_2 - h_1}{\Delta t_1}t\right) + \dots + \left(\sigma\left(t - \sum_{i=1}^{n-2} \Delta t_i\right) - \sigma\left(t - \sum_{i=1}^{n-1} \Delta t_i\right)\right) \cdot \left(h_{n-1} + \frac{h_n - h_{n-1}}{\Delta t_{n-1}}\left(t - \sum_{i=1}^{n-2} \Delta t_i\right)\right)
$$
\n(139)

$$
Z^{ad} = R_{*}^{ad} + \frac{1}{j\omega^{ad}C_{id}^{ad} + \frac{1}{R_{id}^{ad}}}
$$
\n(137)
\nwhose Nyquist plot is an ideal semi-circle, as shown in Figure 11(C), representing the charge transfer reaction.
\nFinally, when $\omega^{ad} > \omega_{\omega}^{ad}$, Eq. (137) is reduced to,
\n
$$
Z^{ad} = R_{*}^{ad} + \frac{1}{j\omega^{ad}C_{id}^{ad}}
$$
\n(138)
\nwhose Nyquist plot is a straight line representing the EDL charging process, as shown in Figure 11(B).
\n**5.2 Numerical Methods of Impedance Calculation**
\nIn this section, we introduce the methods of calculating the impedance from time-domain data, which can be obtained from models and experiments. Firstly, the rank Fourier transform (FFT), another often used numerical method, is introduced briefly.
\nThen it is used to calculate the impedance of the deposition reaction of metal ions. Lastly, the fast Fourier transform
\nApplying linear interpolation to time-domain signal, we obtain
\n
$$
\hat{h}(t) = \left[\sigma(t) - \sigma\left(t - \sum_{i=1}^{r} \Delta t_i\right)\right] \cdot \left[h_1 + \frac{h_2 - h_1}{\Delta t_1}t\right] + ... + \left[\sigma\left(t - \sum_{i=1}^{r-1} \Delta t_i\right) - \sigma\left(t - \sum_{i=1}^{r-1} \Delta t_i\right)\right] \cdot \left[h_{s-1} + \frac{h_{s-1} - h_{s-1}}{\Delta t_{s-1}}\left(t - \sum_{i=1}^{r-2} \Delta t_i\right)\right]
$$
\n(139)
\nwhere $h(t)$ is the recorded time-domain signal, $\sigma(t)$ the normalized step function. Then applying Fourier transform
\nto Eq. (139) gives,
\n
$$
\hat{H}(\omega) = \int_0^{\infty} \hat{h}(t) \exp(-j\omega t) dt
$$
\n
$$
= \frac{1}{j\omega} \left\langle h_1 - h_s \exp\left(-j\omega \sum_{i=1}^{r-1} \Delta t_i\right) \right| - \frac{1}{\omega^2} \left\langle \frac{h_2 - h_1}{\Delta t_1} - \frac{h_s - h_{s-1}}{\Delta t_1} \exp\left(-j\omega \sum_{i=1}^{r-1} \Delta t_i\right)\right|
$$
\n(140)
\nwhere the specific derivatives are detailed below. Integrating the last term

obtained from models and experiments. Firstly, the method of an analytical Fourier transform (AFT) is introduced⁵⁹.
Then it is used to calculate the impedance of the deposition reaction of metal ions. Lastly, the fast Fourier transform (FFT), another often used numerical method, is introduced briefly.
5.2.1 Analytical Fourier transform (or
$$
\int \frac{1}{2} \Delta t
$$
,
1. Applying linear interpolation to time-domain signal, we obtain

$$
\hat{h}(t) = \left[\sigma(t) - \sigma \left(t - \sum_{i=1}^{l} \Delta t_i\right)\right] \cdot \left[h_1 + \frac{h_2 - h_1}{\Delta t_i}t\right] + ... + \left[\sigma \left(t - \sum_{i=1}^{n-2} \Delta t_i\right) - \sigma \left(t - \sum_{i=1}^{l} \Delta t_i\right)\right] \cdot \left[h_{n-1} + \frac{h_n - h_{n-1}}{\Delta t_{n-1}}\right] \left(t - \sum_{i=1}^{n-2} \Delta t_i\right)\right]
$$
(139)
where $h(t)$ is the recorded time-domain signal, $\sigma(t)$ the normalized step function. Then applying Fourier transform
to Eq. (139) gives,

$$
\hat{H}(\omega) = \int_0^{\infty} \hat{h}(t) \exp(-j\omega t) dt
$$

$$
= \frac{1}{j\omega} \left[h_1 - h_n \exp\left(-j\omega \sum_{i=1}^{n-1} \Delta t_i\right)\right] - \frac{1}{\omega^2} \left(\frac{h_2 - h_1}{\Delta t_1} - \frac{h_n - h_{n-1}}{\Delta t_{n-1}} \exp\left(-j\omega \sum_{i=1}^{n-2} \Delta t_i\right)\right]
$$
(140)

$$
= \frac{1}{\omega^2} \sum_{i=1}^{n-2} \left(\frac{h_{n+2} - h_{n+1} - h_{n-1}}{\Delta t_{n-1}} \left[\exp\left(-j\omega \sum_{i=1}^{n-2} \Delta t_i\right)\right] - \exp\left(-j\omega \sum_{i=1}^{n-2} \Delta t_i\right)\right] \exp(-j\omega) dt
$$

$$
= \int_0^{\infty} \hat{h}(t) \exp(-j\omega t) dt
$$

$$
= \int_0^{\infty} \left(\sigma(t) - \sum_{i=1}^{n-2} \Delta t_i\right) - \sigma \left(t - \sum_{i=1}^{n-2
$$

(B) $\omega^{\text{nd}} > \omega_{\text{ct}}^{\text{nd}}$, 1×10^6 Hz $\sim 1 \times 10^5$ Hz; (C) $\omega_{\text{d}}^{\text{nd}} < \omega^{\text{nd}} < \omega_{\text{ct}}^{\text{nd}}$, 1×10^4 Hz ~ 10 Hz; (D) $\omega^{\text{nd}} < \omega_{\text{d}}^{\text{nd}}$, 1 Hz $\sim 1 \times 10^{-4}$ Hz. Parameters are $c_0 =$ -1 $D = 1 \times 10^{-10}$ m² s⁻¹. Matlab script of this model is provided in the

$$
\oint_{\frac{1}{2}} \frac{\cos \theta}{20} \underbrace{\cos \theta}_{20} \underbrace{\cos \theta}_{40} \underbrace{\cos \theta}_{60} \underbrace{\cos \theta}_{50} \underbrace{\cos \theta}_{70} \underbrace
$$

$$
\hat{H}_{n-2}(\omega) = \frac{1}{j\omega} h_{n-2} \exp\left(-j\omega \sum_{i=1}^{n-3} \Delta t_i\right) + \frac{1}{\omega^2} \frac{h_{n-1} - h_{n-2}}{\Delta t_{n-2}} \left(\left(\exp\left(-j\omega \sum_{i=1}^{n-2} \Delta t_i\right) - \exp\left(-j\omega \sum_{i=1}^{n-3} \Delta t_i\right) \right) \right) - \frac{1}{j\omega} h_{n-1} \exp\left(-j\omega \sum_{i=1}^{n-2} \Delta t_i\right)
$$

$$
\hat{H}_2(\omega) = \frac{1}{j\omega} h_2 \exp\left(-j\omega \sum_{i=1}^1 \Delta t_i\right) + \frac{1}{\omega^2} \frac{h_3 - h_2}{\Delta t_{n-2}} \left(\left[\exp\left(-j\omega \sum_{i=1}^2 \Delta t_i\right) - \exp\left(-j\omega \sum_{i=1}^1 \Delta t_i\right) \right] \right) - \frac{1}{j\omega} h_3 \exp\left(-j\omega \sum_{i=1}^2 \Delta t_i\right)
$$
\n
$$
\hat{H}_1(\omega) = \frac{1}{j\omega} h_1 + \frac{1}{\omega^2} \frac{h_2 - h_1}{\Delta t_1} \left(\left[\exp\left(-j\omega \sum_{i=1}^1 \Delta t_i\right) - 1 \right] \right) - \frac{1}{j\omega} h_2 \exp\left(-j\omega \sum_{i=1}^1 \Delta t_i\right) \tag{142}
$$

 $r = \frac{1}{j\omega} h_{k-1} \left[\exp\left(-j\omega \sum_{n=1}^{\infty} \Delta t_{n}\right) - \exp\left(-j\omega \sum_{n=1}^{\infty} \Delta t_{n}\right) \left[\frac{1}{\omega^{2}} \frac{h_{k-1} - h_{k-1}}{\Delta t_{k-1}} \right] \left[\exp\left(-j\omega \sum_{n=1}^{\infty} \Delta t_{n}\right) - \exp\left(-j\omega \sum_{n=1}^{\infty} \Delta t_{n}\right) \right]$
 $+ \frac{1}{j\omega} \frac{h_{k-1} - h_{k-1}}{\Delta t_{k-1}} \exp$ $\int \frac{h}{j\omega} \frac{h_{x}-h_{x-1}}{\Delta t_{x-1}} \exp\left[-j\omega \sum_{i=1}^{m-1} \Delta t_{i}\right] \left(\sum_{i=1}^{m-1} \Delta t_{i} - \sum_{i=1}^{m-1} \Delta t_{i}\right]$

Similarly, we obtain the frequency-domain expression for each term of Eq. (139),
 $\int \Delta t_{x,0} = \int \frac{h_{x,0}}{\omega} \frac{1}{2} \$ $+\frac{1}{j\omega}\frac{\alpha_{m} - \alpha_{m}}{\Delta t_{c+1}}\exp\left[-j\omega\sum_{i}\Delta t_{i}\right]\left[\sum_{i}\Delta t_{i} - \sum_{i}\Delta t_{i}\right]$ (141)

Similarly, we obtain the frequency-domain expression for each term of Eq. (139),
 $\theta_{r,s}(\omega) = \frac{1}{j\omega}h_{s,s} \exp\left[-j\omega\sum_{i=1}^{m}\Delta t_{i}\right] + \frac{1}{$ Similarly, we obtain the frequency-domain expression for each term of Eq. (139),
 $\hat{H}_{w2}(\omega) = \frac{1}{j\omega} h_{x2} \exp\left(-j\omega \sum_{i=1}^{n} \Delta t_i\right) + \frac{1}{\omega^2} \frac{h_{x2} - h_{z2}}{\Delta t_2} \left(\left[\exp\left(-j\omega \sum_{i=1}^{n} \Delta t_i\right) - \exp\left(-j\omega \sum_{i=1}^{n} \Delta t_i\right)\right$ $\left\{\left(\exp\left(-j\omega\sum_{i=1}^{n-2}\Delta t_i\right)-\exp\left(-j\omega\sum_{i=1}^{n-3}\Delta t_i\right)\right)\right\}\right\}$ $\frac{1}{j\omega}h_{n-1}\exp\left(-j\omega\sum_{i=1}^{n-2}\Delta t_i\right)$
 $\exp\left(-j\omega\sum_{i=1}^{2}\Delta t_i\right)-\exp\left(-j\omega\sum_{i=1}^{2}\Delta t_i\right)\right)$ $\left\{-j\omega\sum_{i=1}^{2}\Delta t_i\right\}$
 $\left\{-1\right\}\right\}$ $\left\{-j\omega\sum_{i=$ region. $\sum_{i=0}^{\infty} \frac{1}{j\omega} h_{\infty} \exp\left(-j\omega \sum_{i=1}^{\infty} \Delta t_i\right) + \frac{1}{\omega^2} \frac{h_{\infty} - h_{\infty}}{\Delta t_{\infty}} \left(\left[\exp\left(-j\omega \sum_{i=1}^{\infty} \Delta t_i\right) - \exp\left(-j\omega \sum_{i=1}^{\infty} \Delta t_i\right)\right]\right) - \frac{1}{j\omega} h_{\infty} \exp\left(-j\omega \sum_{i=1}^{\infty} \Delta t_i\right)$
 $(\omega) = \frac{1}{j\omega} h_2 \exp\left(\hat{B}_{1,0}(0) = \frac{1}{j\omega} h_1 \exp\left(-j\omega \sum_{k=1}^{n} \Delta k_1\right) + \frac{h_2 - h_1}{\omega^2} \left(\left[\exp\left(-j\omega \sum_{k=1}^{n} \Delta k_2\right) - \exp\left(-j\omega \sum_{k=1}^{n} \Delta k_1\right)\right]\right) - \frac{1}{j\omega} h_1 \exp\left(-j\omega \sum_{k=1}^{n} \Delta k_1\right)$
 $\hat{H}_1(\omega) = \frac{1}{j\omega} h_1 + \frac{1}{\omega^2} \frac{h_2 - h_1}{\omega^2}$
 $\hat{H}_2(\omega) = \frac{1}{j\omega} h_2 \exp\left(\frac{1}{2}\omega \frac{1}{r_1} \Delta t_i\right) + \frac{1}{\omega^2} \frac{h_2 - h_1}{\Delta t_{c2}} \left(\left[\exp\left(\frac{1}{2}\omega \sum_{k=1}^2 \Delta t_i\right) - \exp\left(\frac{1}{2}\omega \sum_{k=1}^2 \Delta t_i\right)\right)\right) - \frac{1}{j\omega} h_2 \exp\left(\frac{1}{2}\omega \sum_{k=1}^2 \Delta t_i\right)$
 $\hat{H}_1(\omega) = \frac{1}{j\omega} h_1 +$ (ω) = $\frac{1}{j\omega}h_1 + \frac{1}{\omega^2} - \frac{h_1 - h_1}{\Delta t_1} / (\exp[\frac{1}{j\omega} \sum_{x=1}^{n} \Delta t_x] - 1] - \frac{1}{j\omega}h_2 \exp[\frac{1}{j\omega} \sum_{x=1}^{n} \Delta t_x]$ (142)

dding up all terms from $\hat{H}_1(\omega)$ to $\hat{H}_{\omega}(\omega)$, we obtain Eq. (140).

2. Application $\hat{H}_1(\omega) = \frac{1}{1\omega} h_x = \frac{1}{\omega^2} \frac{m_x}{\Delta t_1} \left[|\exp| \frac{1}{2\omega} \sum_i \Delta t_i| -1| \right] - \frac{1}{1\omega} h_z \exp| \frac{1}{2\omega} \sum_i \Delta t_i|$ (142)

Adding up all terms from $\hat{H}_1(\omega)$ to $\hat{H}_2(\omega)$, we obtain Eq. (140).

S.2.2 Application of AFT

Figur

6 Conclusions

(a. *Electrochem.*) 2022, 28(2), 2108471 (27 of 30)

models). Exposition of these models begins with

physical insights, followed by detailed mathematical

derivation, formal analysis, and then practical numeri-

cal impl **Expectition of** the Alexander von Humboldt Foundation.

This canding the Square, numerical

derivation, formal analysis, followed by detailed mathematical

derivation of these models begins with
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 $\frac{d}{dx}$
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Acknowledgements:

Notes:

interests.

implementation with the Matdab scripts provided

is a physical model for the specific system under
 $\frac{1}{2}$ is a physical model of the specific system under

Eld development procedure presented here with
 $\frac{1}{2}$ is In the supporting information. A viable attempt to $\frac{1}{2}$ is $\frac{1}{2}$ is $\frac{1}{2}$ and $\frac{1}{2}$ comparis B a physical model for the specific system under

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¹s own investigation could start with following the

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and analytical impeduate responses to F-10 0 mo and Wedgements:**
 and yier 2 can denote the capacital mate of the mass of the simulation and scheme and in each is finance expressed in Eq. (127). Parameters used in This work is finance in the scheme of China (2180217 This work is financially supported by National and calculation are as follows, $c_0 = 100$ med. m^2 , $k_1 = 4.45 \times 10^{-5}$

Natural Science Foundation of China (21802170) and $\frac{1}{1000} \times \frac{1}{3}$, $D = 3.2 \times 10^{-1}$ m², s Natural Science Foundation of China (21802170) and contribution in ex onews is expressed to the alexander von Humboldt Foundation.

the Alexander von Humboldt Foundation.

Notes:

The authors declare no competing financia (b) Hermander von Humboldt Foundation.

State⁵ Hz, sampling elequency: 100⁶ (excitation frequency),
 Notes:

The authors declare no competing financial Malab seript of this model is provided in the supporting

implie $^{-1}$ D = 3.2×10⁻¹¹ m² · s⁻¹ frequency range: 4.22×10⁻⁴ ~ information.

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- **Notes:**

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The authors declare no competing financial Mathb script of this model is provided in the supporting

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平衡、非平衡、交流状态下电化学双电层 建模的初学者指南 _{电化学(*J. Electrochem.*) 2022, 28(2), 2108471 (30 of 30)
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:平衡、交流状态下电化学双电层}

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摘要: 本文定位在一篇电化学双电层(EDL)理论建模方面入门级文章。我们首先简要介绍了 EDL 的基本特征,简 述了 EDL 理论建模的发展历史袁特别是 D.C. Grahame 之后近几十年的发展历史^遥 然后袁我们依次介绍了平衡状 态和动态下不同复杂度的 EDL 模型。作为一篇入门级文章,我们尽可能详细地阐释理论模型的物理图像、假设、 数学推导、形式分析、数值分析,并附上 Matlab 仿真代码。平衡状态下的模型包括 Gouy-Chapman-Stern(GCS)模 型, Bikerman-Poisson-Boltzmann(BPB)模型, 和非对称离子尺寸模型。我们强调 GCS 模型和 BPB 模型在处理离 子有限尺寸上存在一个微妙的不同。GCS 模型通过人为引入 Helmholtz 平面来考虑离子有限尺寸, 但在 Helmholtz 平面内及弥散层内却依然采用没有考虑离子尺寸效应的 Poisson-Boltzmann 理论, 因而此处的离子浓 度可以无限大。与之不同,BPB 模型通过格子气体方法,能够自洽描述离子有限尺寸效应。不同以往直接采用 Poisson-Nernst-Planck 方程描述 EDL 动态行为,我们从 EDL 的巨势出发,运用基本的泛函分析方法,推导了一个 考虑离子有限尺寸的 EDL 动态模型。这一理论方法拓展性好。读者可以根据研究对象的需要,建立不同复杂度的 EDL 动态模型。最后,我们基于 EDL 动态模型,推导了 EDL 的电化学阻抗谱理论模型,以试图向读者展示如何从 一个时域物理模型出发,推导相应的阻抗谱物理模型。读者若想要踏进理论电化学这个美丽的花园,根据我们自 己学习和研究的经验,一个可行的方式是拿起纸和笔来开始推导本文所介绍的这些模型。 关键词: 双电层:平衡;非平衡;电化学阻抗谱;物理建模