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Hamzah Hisham

Denuault Guy

Bartlett Philip

Chemistry, University of Southampton, Southampton, SO171AL, UK; p.n.bartlett@soton.ac.uk

Pinczewska Aleksandra

Kilburn Jeremy

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Electrografting of Mono-N-Boc-Ethylenediamine from an Acetonitrile/Aqueous NaHCO₃ Mixture

Hisham Hamzah¹, Guy Denuault¹, Philip Bartlett^{1*},
Aleksandra Pinczewska², Jeremy Kilburn³

(1. Chemistry, University of Southampton, Southampton, SO17 1BJ, UK; 2. School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London, E1 4NS, UK; 3. King's College, The University of Aberdeen, Aberdeen, AB24 3FX, UK)

Abstract: The electrografting of primary amines to carbon electrodes is now widely employed for electrode modification. Using a mixture of acetonitrile and 0.1 mol·L⁻¹ aqueous sodium hydrogen carbonate (NaHCO₃) in the ratio of 4:1, the efficiency for coupling of mono-N-Boc-ethylenediamine (EDA-Boc) on the surface of glassy carbon was significantly improved as compared with that obtained using acetonitrile alone. In the presence of NaHCO₃, the initial current determined in the cyclic voltammogram became higher, and the layer of attached amine was formed more rapidly, accordingly, the electrode was passivated more rapidly. The resulting film of EDA-Boc was shown to be more severely blocking toward the electrochemical reaction of [Fe(CN)₆]³⁻. Following removal of the Boc protecting group and coupling of the free amine to anthraquinone-2-carboxylic acid, a higher surface coverage of the anthraquinone was obtained. Modelling for the electrografting reaction using a simple kinetic scheme, it was demonstrated that the simulated voltammograms agreed well with the experimentally measured voltammograms. Comparison between the model fitting parameters obtained from the acetonitrile alone and the acetonitrile/NaHCO₃ mixture showed that the competition between reaction of the amine radicals with the carbon surface and reaction in the homogeneous solution became more favourable for the surface reaction in the acetonitrile/NaHCO₃ mixture.

Key words: electrografting; mono-N-Boc-ethylenediamine; amine oxidation; glassy carbon; surface modification

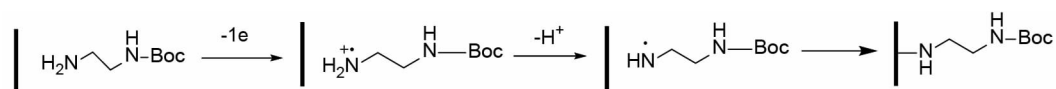
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The electrochemical attachment of primary amines at carbon electrodes is an attractive method for the systematic modification of electrodes. The process is efficient and leads to the formation of a strong carbon-nitrogen bond formed by reaction of the product of the one electron oxidation process at the surface^[1-3]. Passivation of the electrode surface is observed during the reaction, and on cycling the magnitude of subsequent oxidation peaks decreases. Secondary amines are significantly less reactive and tertiary amines do not react with the electrode surface, most likely due to steric hindrance^[4]. The electrografting of primary amines has been shown to involve sequential one electron oxidation to create an unstable cation radical followed by the rate limiting depro-

tonation to form the neutral radical^[5] (Scheme 1). Studies on deuterated species showed that the neutral radical, formed after the deprotonation step, reacts with sp² carbon at the glassy carbon (GC) surface to form a stable covalent bond^[1]. However, limited studies have been reported on the effect of the chemical deprotonation step on the overall rate of the amine attachment.

Electrooxidation of primary amines has been mainly carried out in organic solvents such as dimethylformamide, acetonitrile (ACN) and ethanol^[1-2, 6]. Usually acetonitrile is chosen as a medium for amine electrografting due to its high polarity, relatively basic character as compared to other aprotic solvents and electrochemical stability at the higher potentials usually



Scheme 1 Established mechanistic sequence taking place during the electrochemical oxidation of primary amines in non-aqueous solvents

required for formation of the amine radical cation.

A number of studies about the attachment of aromatic primary amines in organic medium with the addition of aromatic base in order to increase the rate determining deprotonation step have been reported. Successful preparation of modified electrodes with aromatic primary amines was achieved in the presence of trimethylaminopyridine^[7-9]. Amatore et al. described the attachment of π -conjugated ferrocifen amine at GC where the addition of trimethylpyridine base affected the deprotonation step observed by the decrease of oxidation potential and the loss of amine reversibility in comparison to the oxidation of the same amine without the presence of the aromatic base^[8]. However, addition of the aromatic amine base did not increase the surface coverage of the primary aliphatic amine bearing ferrocene functionality at the carbon electrodes^[10].

Use of aqueous media such as phosphate or sodium hydrogen carbonate buffers is limited due to problems of water oxidation occurring at higher potentials which can compete with the amine radical formation. Recent work by Geneste et al.^[11] described the primary amine attachment at polymerised photoresist carbon films in aqueous sodium hydrogen carbonate solutions and compared the result with attachment of the same amines in organic medium. Their results indicated that the relatively lower coverage of the amines was achieved by electrolysis in aqueous basic solution in comparison with the attachment carried out under the same conditions in acetonitrile. The lower efficiency of the amine attachment in the carbonate buffer was explained by the lower amount of the amine radical electrogenerated in close vicinity of the electrode and the higher number of possible side products formed in the aqueous solution^[12].

In this work we have investigated the electro-

grafting of aliphatic primary amines using an acetonitrile/sodium hydrogen carbonate mixture as the initial studies showed significantly higher coverage when compared to neat acetonitrile.

Studies of the electrooxidation were carried out using mono-N-Boc-ethylenediamine (EDA-Boc) as a model system. Recent work by Bartlett et al. has shown that the monolayers of EDA-Boc at glassy carbon and carbon nanotube electrodes could be formed by electrochemical oxidation of EDA-Boc in acetonitrile^[13-16]. After removal of the Boc group further chemical modification steps allow the introduction of different redox probes and spacers to achieve a high level of control over the modification of the carbon surface, and hence, its electrocatalytic properties. This approach was successfully utilised in the design and fabrication of electrodes for the electrocatalytic oxidation of NADH and for laccase catalysed oxygen reduction^[17-18].

1 Experimental

1.1 Materials and Reagents

All the reagents for the electrochemical experiments were used as received without further purification. Acetonitrile (ACN) was HPLC grade (Fisher Scientific), the aqueous solution of 0.1 mol · L⁻¹ sodium hydrogen carbonate (Sigma Aldrich) was prepared using water from a Millipore Milli-Q water purification system. Mono-N-Boc-ethylenediamine (EDA-Boc), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) were purchased from Sigma-Aldrich and used without further purification.

All the electrochemical experiments were carried out in standard glass 3-neck electrochemical cells using a μ -AutoLab III potentiostat/galvanostat (Metrohm UK Ltd.). Working electrodes were glassy carbon rods (3 mm diameter, SIGRADUR® G Glassy Carbon HTW) sealed in glass tube and connected with

copper wire using indium. The glassy carbon rods protruded several mm beyond the end of the glass tube and we used a meniscus contact^[19] with the solution for all the electrochemical experiments as this was found to give better repeatability between replicate experiments. The counter electrode was a platinum mesh (1 cm²) and the reference electrode either a homemade saturated calomel electrode or a homemade Ag/AgCl electrode in 3 mol·L⁻¹ KCl. Prior to modification, the glassy carbon electrodes were polished using a silicon carbide polishing paper (grad 1200) followed by a 5 μm lapping film. The glassy carbon electrodes were then polished with 0.1 and 0.3 μm alumina slurries on polishing cloth pads (Buehler). The polished glassy carbon electrodes were sonicated with deionized water for 7 min and dried in air. They were then sonicated in ethanol for 10 min and dried in air.

1.2 Coupling of Anthraquinone-2-Carboxylic Acid to EDA Modified GC Electrodes

The Boc-protecting group was removed by suspending the modified electrodes in 4 mol·L⁻¹ HCl in dioxane solution at room temperature with stirring for 1 h. The electrodes were then washed thoroughly with water and ACN, and dried. They were then immersed in 6 mL of DMF solution containing 10 mg anthraquinone-2-carboxylic acid (AQ), 480 μL EDC and 68.4 mg of NHS at room temperature with stirring for 16 h. The modified electrodes were then washed thoroughly with deionised water and ACN, and dried. The AQ modified GC electrodes were stirred in DMF for 3 days in order to remove any adsorbed AQ before the electrochemical characterisation.

2 Results and Discussion

2.1 Electrografting of EDA-Boc

Mono-N-Boc-ethylenediamine (EDA-Boc) is a short, aliphatic primary amine which forms uniform packed organic monolayers upon attachment at GC by electrooxidation in neat ACN^[13-14, 16]. The EDA-Boc gives a well-defined oxidation peak in ACN at ~1.5 V vs. Ag/AgCl that corresponds to formation of the

amine radical. Attachment to the GC surface occurs by reaction of the radical with sp² carbon at the electrode surface. The reaction is accompanied by a significant decrease of the anodic current in the second and following scans with passivation of the electrode surface after 2 ~ 4 scans.

Fig. 1 shows a comparison on the voltammetric curves for the oxidation of the amine in ACN, ACN containing sodium hydrogen carbonate (4:1 ACN to 0.1 mol·L⁻¹ aqueous NaHCO₃) and in ACN containing water (4:1 ACN to water). The voltammograms shown are representative of many replicate experiments. Distinct differences are clear in the shapes of the anodic peaks and in the values of the currents for the first and following cycles.

The current during the first cycle is lower for neat ACN in comparison to that in ACN/NaHCO₃ although the oxidation peaks for the amine appear around 1.5 V vs. Ag/AgCl in both cases. This suggests that more of the amine cation radical is formed in the presence of NaHCO₃. The following cycles show that the current decreases in both cases but for the neat ACN 3 cycles are required to fully block the oxidation of EDA-Boc at 1.5 V, whereas for the ACN/NaHCO₃ mixture the blocking occurs more rapidly and the peak at 1.5 V is absent on the second cycle. Note that a persistent, increasing background is observed from around 1.5 V vs. Ag/AgCl during the second and subsequent cycles. The data for the oxidation of the EDA-Boc in a mixture of ACN and water, as seen in Fig. 1C, show similar passivation behavior with a peak on the initial scan again at 1.5 V. The voltammetric curve for the ACN/water mixture resembles that for neat ACN more closely than that for ACN/NaHCO₃, indicating that the base is having a distinct effect and it is not just the result of the added water. The results suggest that the addition of NaHCO₃ favours the coupling of the amine to the carbon surface. It should be noted that in all cases the charge passed during the cycling is many times greater than that required to form a monolayer of amine attached to the surface (~10 mC·cm², compared to 0.4 mC·cm²) because many of the radicals generated undergo other

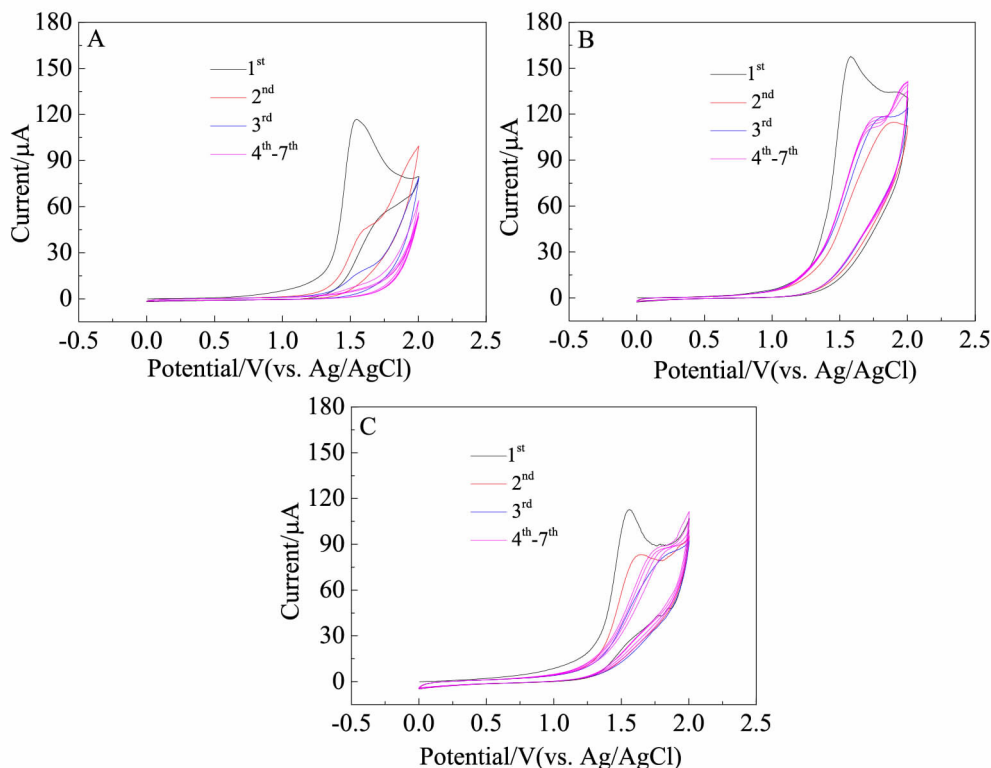


Fig. 1 Cyclic voltammograms recorded for $10 \text{ mmol} \cdot \text{L}^{-1}$ EDA-Boc with $0.1 \text{ mol} \cdot \text{L}^{-1}$ TBATFB carried out in neat ACN (A), 20% NaHCO_3 in ACN (B) and 20% water in ACN (C). All the experiments were recorded at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$ for 7 cycles, electrode area 0.071 cm^2 .

reactions in the solution.

2.2 Blocking by Immobilised EDA-Boc

The cyclic voltammetry of electroactive solution species provides a convenient technique to study the presence of the grafted films and their blocking properties on the electrode surface. As shown in Fig. 2, the voltammogram of $[\text{Fe}(\text{CN})_6]^{3-}$ shows near reversible voltammetric response (blue line) at the bare GC electrode with a redox potential of $\sim 190 \text{ mV}$ vs. SCE. However, after electrografting the voltammetric response is significantly blocked by the EDA-Boc films on the electrode surface. This leads to an increase in the peak separation and a decrease in the peak currents; greater blocking by the surface film results in a larger ΔE_p value. The black and red voltammograms in Fig. 2 show the behaviors at EDA-Boc films prepared in ACN and ACN/ NaHCO_3 respectively. It is clear that the film formed in ACN/ NaHCO_3 is more blocking toward the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ couple than the film formed in neat ACN.

Electrochemical impedance spectroscopy (EIS) provides a complimentary technique to evaluate the blocking nature of the EDA-Boc film^[6]. Fig. 3 shows the EIS results for the bare GC electrode and the electrode coated with EDA-Boc from ACN and ACN/

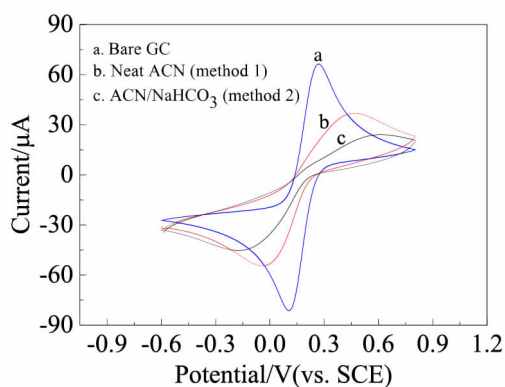


Fig. 2 Voltammograms for $10 \text{ mmol} \cdot \text{L}^{-1}$ $\text{K}_3[\text{Fe}(\text{CN})_6]$ in $0.1 \text{ mol} \cdot \text{L}^{-1}$ KCl showing the blocking effect at EDA-Boc modified GC electrodes. Scan rate = $50 \text{ mV} \cdot \text{s}^{-1}$, electrode area = 0.071 cm^2 , in each case the second cycle is shown.

NaHCO₃. The Nyquist plots have the expected shape for a simple solution redox process of a semicircle and a 45° Warburg line at low frequency^[20-21]. The diameter of the semicircle corresponds to the charge-transfer resistance (R_{ct}), and it is very clear that this increases in going from the bare GC electrode, to the EDA-Boc coated electrode prepared in ACN, to that prepared in ACN/NaHCO₃. The EIS results agree with those from voltammetric data: the electrografted EDA-Boc film produced from the ACN/NaHCO₃ solution is the most blocking among the three.

2.3 Coupling of AQ to the EDA Modified GC Electrodes

The ultimate purpose of electrografting the mono-amine EDA-Boc and similar mono-Boc protected diamines to the carbon electrode surface is to use them as linkers in a synthetic strategy for the rational modification of carbon electrode surfaces^[13, 16, 19]. Therefore, to test whether the films grown in the ACN/NaHCO₃ solution were better for this purpose we removed the Boc protecting group and then coupled the free amines to anthraquinone-2-carboxylic acid. This coupling reaction has been studied in detail in earlier work^[13, 16, 22]. Fig. 4 shows replicate results for 6 electrodes, 3 prepared by mono-amine EDA-Boc

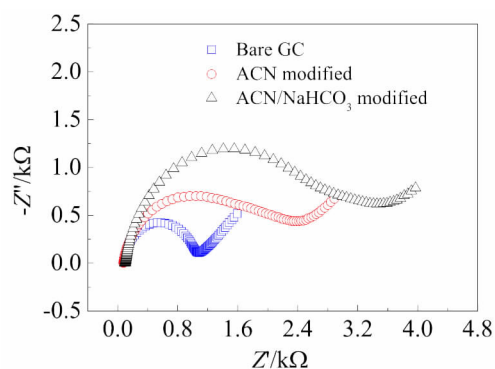


Fig. 3 Nyquist plots of the impedance spectra recorded at 0.188 V vs. SCE in 10 mmol·L⁻¹ of K₃[Fe(CN)₆] and 0.1 mol·L⁻¹ KCl for bare GC electrode (blue), GC electrode modified with EDA-Boc film by electrografting in ACN (red), and GC electrode modified with EDA-Boc film by electrografting in ACN/NaHCO₃ (black). Frequency range 0.1 kHz to 100 kHz, modulation amplitude 5 mV.

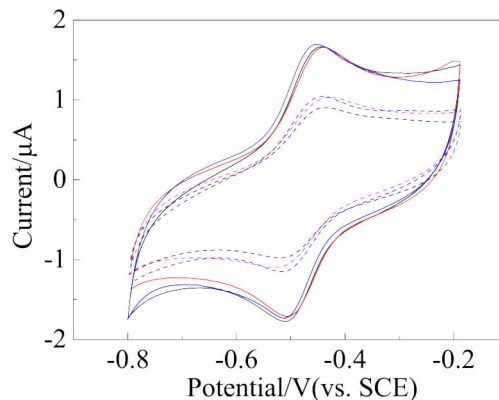


Fig. 4 Voltammograms from six AQ modified GC electrodes in 0.1 mol·L⁻¹ phosphate buffer, pH 7 (scan rate = 50 mV·s⁻¹, electrode area = 0.071 cm², the sixth cycle is shown). The dashed lines are for electrodes prepared by electrografting the EDA-Boc linker from ACN, the solid lines are for electrodes prepared by electrografting from ACN/NaHCO₃; all other conditions were the same.

electrografting in ACN and 3 in ACN/NaHCO₃.

The dashed lines are the voltammograms for AQ attached to the EDA linker grafted in ACN, the solid lines for those with NaHCO₃ added to the electrografting solution. The peaks around -0.45 V vs. SCE correspond to the oxidation and reduction of the bound anthraquinone. It is clear that the coverage is significantly greater for the films electrografted from ACN/NaHCO₃ (181 ± 11.9 pmol·cm⁻² as compared to 112 ± 3.54 pmol·cm⁻²), again, consistent with more efficient electrografting from the solution with the added NaHCO₃.

2.4 Modelling of the Electrografting Reaction

In its simplest form the electrografting reaction can be represented by the following three steps:



In Step (1), the electrochemical oxidation of EDA-Boc, **A**, produces the reactive intermediate **B**. In Step (2), **B** reacts with the electrode surface, to form **C** which adsorbs and blocks further reaction. As the coverage of **C** increases the amount of free surface

available for reaction decreases; this is the basis of the inhibition process. In Step (3), the reactive intermediate **B** undergoes a homogeneous reaction in solution. The parameters, k_s , α , E^0 , k_a , and k_h , are, respectively, the standard rate constant for electron transfer, transfer coefficient, standard potential, rate constant for adsorption and rate constant for the homogeneous reaction. The overall mechanism is represented mathematically and numerically as detailed in Appendix 1. This model follows that proposed by Bhugun and Savéant^[23] for the formation of blocking films at electrode surfaces by diazonium reduction and aryl radical coupling at the surface.

In this model, the voltammogram for the first cycle and the significant current decrease over subsequent cycles are determined by several electrochemical parameters which describe the kinetic competition of radical species at the surface (k_a) to solution reactions (k_h), the diffusion coefficient of the substrate (D_A) and the coverage of the inhibiting species (Γ).

Savéant and co-workers^[23-24] presented a theoretical model to analyse self-inhibition reactions from simple repetitive cyclic voltammetry and to predict how the film forms with time in preparative-scale electrolysis. In their analytical model they assume that the homogenous reaction is very fast, hence they ignore the loss of **B** by diffusion into the bulk solution. We have modelled the behavior, including diffusion of **B** into the bulk, using simulation code written in MATLAB (see Appendix 1).

To apply the model we need to specify the parameters E^0 , D_A , Γ_{\max} , k_a , k_h , α and k_s . In order to determine the diffusion coefficient, D_A , for the EDA-Boc in the different solutions we made chronoamperometric measurements and used the Cottrell equation to analyse data from the first 2 s after the potential step at a freshly polished electrode. In this way, the effect of the blocking reaction is minimal. The values for the diffusion coefficient of EDA-Boc in the three solutions were found to be $4.84 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, $7.42 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ and $5.70 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, respectively, for ACN, ACN/NaHCO₃ and ACN/water. Notice that this trend matches heights of the peak currents for the first cycles in the voltammetric measurements in each case (compare in Fig. 1).

2.5 Comparison of Modelled and Experimental Results

In each case three replicate experiments were performed and were found to be in close agreement. In the plots only one of the replicates is shown. Fig. 5 shows the first seven voltammetric cycles for the electrochemical grafting of EDA-Boc in ACN. The corresponding simulated voltammograms from the model are also shown. Both the experimental data and the simulation reveal the blocking of the electrode surface by the EDA-Boc film taking place after three cycles.

The fitting values used for the simulation, Table 1, were obtained by manually varying the values. The maximum coverage, Γ_{\max} , was taken as 2.0×10^{-9}

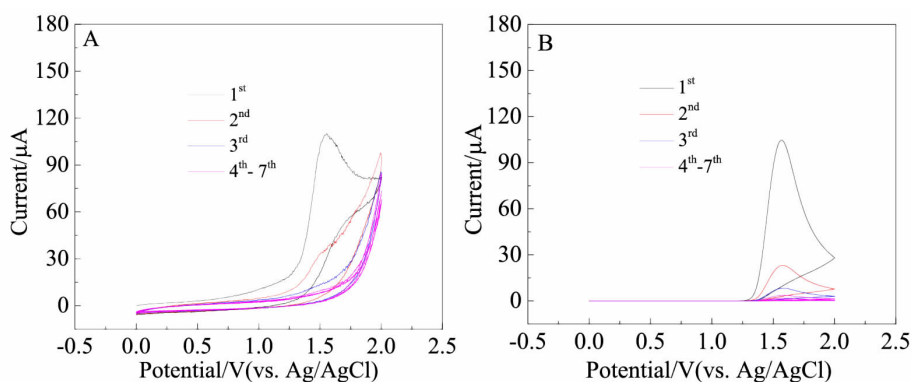


Fig. 5 A. First seven scans for electrografting in $10 \text{ mmol} \cdot \text{L}^{-1}$ EDA-Boc with $0.1 \text{ mol} \cdot \text{L}^{-1}$ TBATFB in neat ACN. Scan rate = $50 \text{ mV} \cdot \text{s}^{-1}$, electrode area = 0.071 cm^2 ; B. Simulation curves using $D_A = 4.9 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, $\Gamma_{\max} = 2.0 \times 10^{-9} \text{ mol} \cdot \text{cm}^{-2}$, $k_s = 1.3 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1}$, $k_a = 1.95 \times 10^{-5} \text{ cm} \cdot \text{s}^{-1}$, $k_h = 0.6 \text{ s}^{-1}$, $\alpha = 0.7$, $E^0 = 1.48 \text{ V}$.

mol·cm² for EDA-Boc and the value of k_s was taken as $1.3 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1}$, of the same order of magnitude as that reported by Adenier et al.^[3] from simulation of the voltammetry for electrochemical oxidation of secondary and tertiary aliphatic amines. The values of E^0 , k_s and α directly affect the position and width of the voltammetric peak. The parameters k_a and k_h directly affect its height, and the relative sizes of the first, second and subsequent peaks. The efficiency of the passivation reaction is determined by the balance of the fates of the reactive species **B** that can react at the electrode surface, or react with species in solution, or diffuse into the bulk. As explained by Bhugun and Savéant^[23], the competition between coupling of **B** to the electrode surface and reaction in solution is described by the ratio of the heterogeneous rate constants k_a and $(D_A k_h)^{1/2}$. In the present case, $k_a \ll (D_A k_h)^{1/2}$, and therefore, it is the ratio $k_a/k_h^{1/2}$ which determines the fitting rather than the individual values of the two rate constants.

A very clear difference between the experiment and the simulation is that in the experiment there is a significant residual background current that increases rapidly with potential above 1.5 V. To explore the origin of this background current we recorded voltammograms for the passivated electrodes in different solutions. Fig. 6 shows the voltammetric curves for a bare GC (blue) and an EDA-Boc modified GC electrode (red) in ACN solution. In both cases the background current is low compared to that for the EDA-Boc modified electrode in the ACN containing EDA-Boc solution (black curve). It is clear that

the EDA-Boc contributes significantly to this background.

This background current is not included in the simulation. To include its effect, and facilitate the comparison of the simulation with experiment, we have used the experimental background current measured from the fourth to seventh voltammetric scans and added this to the simulated current from the model. Fig. 7 shows an example to illustrate this approach. When the experimentally determined background currents are included in the simulation, the experimental and simulated voltammograms show good agreement (Fig. 8). The same approach was applied to modelling the cyclic voltammograms for electrografting of EDA-Boc in the ACN/NaHCO₃ mixture, as presented in Fig. 9. The corresponding parameters used in the model are given in Table 1. Again, there is satisfactory agreement between the experimental results and the simulation data once the background is included.

The sensitivity of the fit to the value of the ratio $k_a/k_h^{1/2}$ is shown in Fig. 10, where we keep k_h constant and vary k_a . As expected, for larger $k_a/k_h^{1/2}$ the surface is blocked more rapidly and the height of the peak current of the first scan decreases, in addition the current on the second cycle (not shown) gradually decreases until the peak disappears. From Fig. 10 we find that the best fit corresponds to the value of $k_a/k_h^{1/2}$ being $8.3 \times 10^{-5} \text{ cm} \cdot \text{s}^{-1/2}$.

Comparing the fitting parameters in Table 1, it is clear that the difference between the ACN and the ACN/NaHCO₃ is that the value of $k_a/k_h^{1/2}$ is signifi-

Tab. 1 Values for MATLAB parameters obtained from the experiments and used in irreversible CV simulation

Parameter	ACN	ACN/NaHCO ₃
Redox potential (E^0)	1.48 V	1.48 V
Experimental diffusion coefficient	$4.6 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$	$7.42 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$
Diffusion coefficient (D_A) in simulation	$4.9 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$	$7.5 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$
Maximum surface coverage (Γ_{max})	$2.0 \times 10^{-9} \text{ mol} \cdot \text{cm}^{-2}$	$2.0 \times 10^{-9} \text{ mol} \cdot \text{cm}^{-2}$
Rate constant for electron transfer (k_s)	$1.3 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1}$	$1.3 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1}$
Transfer coefficient (α)	0.7	0.7
Rate constant ratio ($k_a/k_h^{1/2}$)	$2.5 \times 10^{-5} \text{ cm} \cdot \text{s}^{-1/2}$	$8.3 \times 10^{-5} \text{ cm} \cdot \text{s}^{-1/2}$

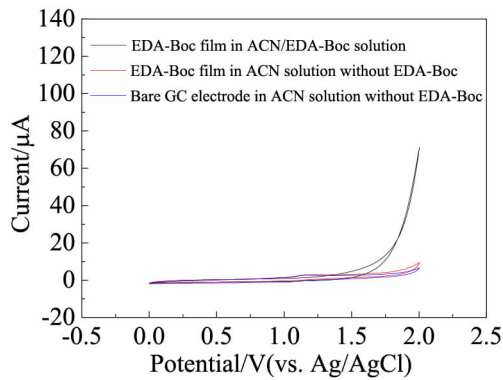


Fig. 6 Voltammograms showing the background currents on bare GC electrode and EDA-Boc modified GC electrodes in different solutions (in each case the third cycle is shown). Scan rate = $50 \text{ mV} \cdot \text{s}^{-1}$, electrode area = 0.071 cm^2 .

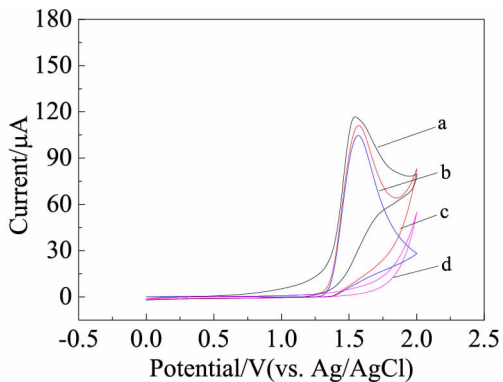


Fig. 7 First cycle experimental (A) and simulated voltammograms (B) for $10 \text{ mmol} \cdot \text{L}^{-1}$ EDA-Boc with $0.1 \text{ mol} \cdot \text{L}^{-1}$ TBATFB in ACN, scan rate = $50 \text{ mV} \cdot \text{s}^{-1}$ and electrode area = 0.071 cm^2 ; C. Background current determined from the fifth experimental cycle; D. Simulated voltammogram with added experimental background current from (C). Simulation parameters $D_A = 4.9 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, $\Gamma_{\text{max}} = 2.0 \times 10^{-9} \text{ mol} \cdot \text{cm}^{-2}$, $k_s = 1.3 \times 10^3 \text{ cm} \cdot \text{s}^{-1}$, $k_a = 1.95 \times 10^5 \text{ cm} \cdot \text{s}^{-1}$, $k_h = 0.6 \text{ s}^{-1}$, $\alpha = 0.7$, $E^0 = 1.48 \text{ V}$.

cantly larger for the ACN/ NaHCO_3 , $8.3 \times 10^{-5} \text{ cm} \cdot \text{s}^{-1/2}$, as compared to $2.55 \times 10^{-5} \text{ cm} \cdot \text{s}^{-1/2}$. Thus, in the presence of base the rate for the attachment of EDA-Boc to the surface of the GC electrode is enhanced. This is most likely because the intermediate radical species **B** reacts less rapidly with solution species in the ACN/ NaHCO_3 solution (k_h smaller), leading to more coupling to the electrode surface.

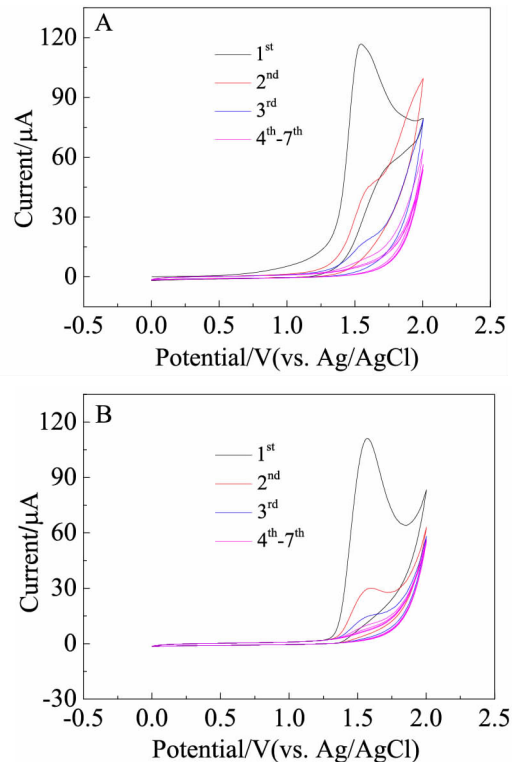


Fig. 8 Experimental (A) and simulated (B) voltammograms for seven cycles of electrografting of EDA-Boc in ACN. The simulated voltammograms include the experimentally determined background currents. Scan rate = $50 \text{ mV} \cdot \text{s}^{-1}$, electrode area = 0.071 cm^2 . Simulation parameters $D_A = 4.9 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, $\Gamma_{\text{max}} = 2.0 \times 10^{-9} \text{ mol} \cdot \text{cm}^{-2}$, $k_s = 1.3 \times 10^3 \text{ cm} \cdot \text{s}^{-1}$, $k_a = 1.95 \times 10^5 \text{ cm} \cdot \text{s}^{-1}$, $k_h = 0.6 \text{ s}^{-1}$, $\alpha = 0.7$, $E^0 = 1.48 \text{ V}$.

3 Conclusions

We have shown that changing from ACN to ACN/ NaHCO_3 (4:1 ACN to $0.1 \text{ mol} \cdot \text{L}^{-1}$ aqueous NaHCO_3) mixture significantly improves the efficiency in coupling of EDA-Boc to the surface of glassy carbon electrodes. In the presence of added NaHCO_3 the initial current measured in cyclic voltammetry is greater because the diffusion coefficient for the EDA-Boc is larger.

Using cyclic voltammetry to study $[\text{Fe}(\text{CN})_6]^{3-}$ in solution, and using impedance measurements, we have shown that the EDA-Boc layers formed in the ACN/ NaHCO_3 solution mixture provide a more significant blocking effect; and using coupling of anthraquinone-2-carboxylic acid to the deprotected layers we have shown that there are significantly more

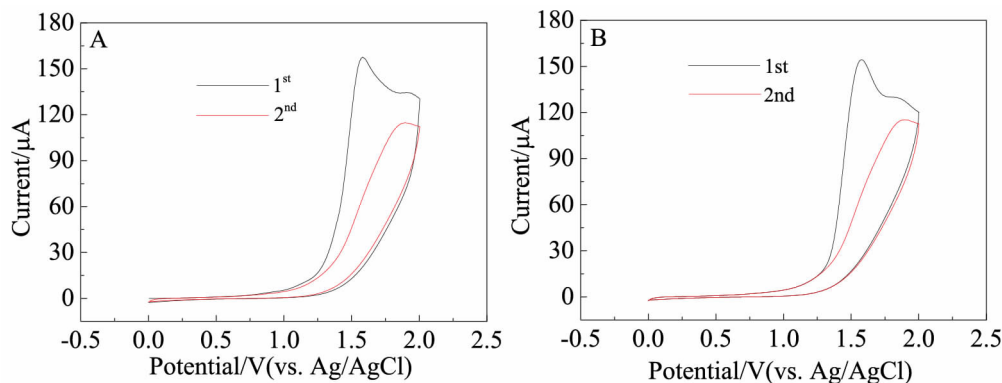


Fig. 9 Experimental (A) and simulated (B) voltammograms for the first two cycles of electrografting of EDA-Boc in ACN/NaHCO₃. The simulated voltammograms include the experimentally determined background currents. Scan rate = 50 mV · s⁻¹, electrode area = 0.071 cm². Simulation parameters $D_A = 7.5 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, $\Gamma_{\text{max}} = 2.0 \times 10^{-9} \text{ mol} \cdot \text{cm}^{-2}$, $k_s = 1.3 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1}$, $k_a = 6.4 \times 10^{-5} \text{ cm} \cdot \text{s}^{-1}$, $k_h = 0.6 \text{ s}^{-1}$, $\alpha = 0.7$, $E^0 = 1.48 \text{ V}$.

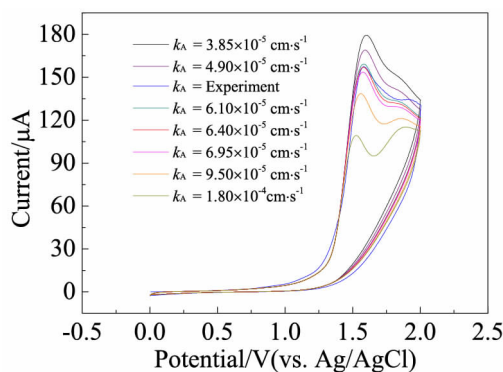


Fig. 10 Comparison of first scan voltammograms for electrografting of EDA-Boc in ACN/NaHCO₃ and simulations calculated for different values of k_a , the other simulation parameters were $D_A = 7.5 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, $\Gamma_{\text{max}} = 2.0 \times 10^{-9} \text{ mol} \cdot \text{cm}^{-2}$, $k_s = 1.3 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1}$, $k_h = 0.6 \text{ s}^{-1}$, $\alpha = 0.7$, $E^0 = 1.48 \text{ V}$. Scan rate = 50 mV · s⁻¹, electrode area = 0.071 cm².

amine groups available for subsequent derivatisation on the surface modification in ACN/NaCO₃. Thus, using the ACN/NaCO₃ has potential practical benefits for the attachment of the Boc protected linker to the carbon surface and we expect that a similar effect should be seen for other mono-Boc protected diamines.

The experimental voltammetric results for the electrografting have been modelled using a simple kinetic model originally proposed by Savéant for diazonium coupling at electrodes. Good agreement between the modelled and experimental results was obtained

when the residual background current was included showing that the simple kinetics scheme adequately describes the process.

Comparison of the fitting parameters for the two cases, the electrografting from ACN and electrografting from ACN/NaHCO₃, shows that there is a significant difference in the ratio of the rate constants for attachment to the surface and reaction in solution $k_a/k_h^{1/2}$, that is probably due to the slower loss of the radical species by reaction in homogeneous solution (lower k_h) in the more basic solution.

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Supporting Information Available:

Appendix I showing modelling for the electrografting reaction using a simple scheme is available free of charge via the Internet at <http://electrochem.xmu.edu.cn>.

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乙腈/碳酸氢钠溶液混合物电嫁接 叔丁氧羟基-乙二胺

Hisham Hamzah¹, Guy Denuault¹, Philip Bartlett^{1*},
Aleksandra Pinczewska², Jeremy Kilburn³

(1. 南安普顿大学化学系, 英国南安普顿, SO17 1AL; 2. 伦敦大学玛丽女王学院, 生物与化学科学学院, 英国伦敦, E1 4NS; 3. 阿伯丁大学国王学院, 英国阿伯丁, AB24 3FX)

摘要: 碳电极表面的伯胺电嫁接被广泛地应用于电极表面改性. 本文通过比较发现, 在比例为 4:1 的乙腈和 $0.1\text{mol}\cdot\text{L}^{-1}$ 碳酸氢钠溶液混合物中, 玻碳电极表面嫁接上叔丁氧羟基-乙二胺的效率比在单纯的乙腈中显著提高. 有碳酸氢钠存在时, 循环伏安测得电极的初始电流增大, 表明电极表面胺嫁接层的形成更快速, 从而使得电极表面更容易钝化, 导致乙二胺-叔丁氧羟基膜层更严重地阻碍 $[\text{Fe}(\text{CN})_6]^{3-}$ 的反应. 通过去除叔丁氧羟基保护层, 在蒽醌-2-羧酸上接自由胺, 可获得较高的蒽醌表面覆盖度. 采用简单动力学模型模拟了电嫁接反应, 结果表明, 模拟得到的循环伏安曲线与实验测得的循环伏安曲线相一致. 对比在单纯乙腈和乙腈/碳酸氢钠溶液混合物中模型拟合得到的参数值可知, 胺自由基与碳表面的反应和在均相溶液中的反应相互竞争, 更有利于乙腈与碳酸氢钠的表面反应.

关键词: 电嫁接; 叔丁氧羟基-乙二胺; 胺氧化; 玻碳电极; 表面修饰