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# A Study on Stochastic Resonance for the Process of Active-passive Transition of Iron in Sulfuric Acid

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**Abstract:** The bistable characteristics of the process of active-passive transition of iron in sulfuric acid was described and the stochastic resonance phenomenon in the process was simulated.

**Key word:** Active-passive transition, Stochastic resonance, Bistability, Electrochemistry

**CLC number:** TG171 **Document code:** A

## 1 Introduction

Passivation of iron in sulfuric acid was observed by Flade in many years ago. Since the seventies, it has been shown that polarization curves of an iron rotating disk electrodes in 1 mol/L sulfuric acid have displayed an hysteresis loop[1~3]. From the nonlinear dynamics point of view, this can be diagnostic of bistable characteristics.

The concept of stochastic resonance (SR) was first put forward in the seminal paper by Benzi and coworkers[4], in where they faced the problem of the periodically recurrent ice ages. The basic ideas in the concept[4,5] are: for a given nonlinear system, which possesses the characteristic of bistability, *i.e.*, more generally, a form of threshold, when there is some coherence between the nonlinear conditions of the system, *i.e.*, input signal and noise, an extra dose of noise can actually be helpful rather that hinder the performance of the system, constituting a kind of coherent effect between the stochastic force and the signal. A specific term, called signal-to-noise ratio (SNR),

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gives quantitatively account for the effect. The concept of SR plays definitely not only theoretical importance ,but also a number of appealing potential applications.

In the research area of electrochemical reactions , much attention has been attracted by non-linear dynamics , such as oscillation and surface pattern[6]. In the relevant literature ,also some reports on electrochemical bistable systems are found[3,7,8]. In this paper ,the experimental results reported by Epelboin et al[1] have been analyzed ,and the bistable model for the process of active-passive transition for iron in sulfuric acid is described. With this model ,SR phenomenon is simulated. Through this way , the concept of SR is introduced into electrochemistry , so that this work may help researchers to find SR phenomenon in electrochemistry experimentally.

## 2 Discription of the bistable model

In the experiment , Epelboin et al[1] recorded a current-votage curve with a 5mm diameter disk ,rotating at 750rpm in 1 mol/L sulfuric acid solution ,which shows a hysteresis loop. In the forward anodic voltage sweep ,the curve *a-b-d-e-h* will be obtained ,while in the backward cathodic scan ,the curve *h-e-f-b-a* is recorded.

In the curve the vertical line *b-f* corresponds to ‘Flade potential’[1]. From the theoretical point of view ,forward and backward polarization curves should be the coincident , *i. e.* ,it should be *a-b-f-h* ≡ *h-f-b-a*. Actually ,due to the ohmic potential drop ,the hysteresis loop is introduced. Therefore ,for a given *cross-sectional area* of the rotating disk electrode ,when the controlling parameter of E (polarization potential) is close to points *f* and *e* ,the polarization curve can be in two possible stable steady states , *i. e.* , *b-d* or *f-e* ,which correspond to active and passive state of the electrode system respectively. Therefore ,from the nonlinear dynamics point of view , it can be viewed as a typical bistable state[9,10]. At a given time ,the system will be in one given state ,which is determined by the initial condition. The differential equation describing the behaviof of the system can be modeled on the experimental data as

$$dI/dt = (I - 1) - (I - 1)^3 \cdots \quad (1)$$

where $I$ represents the current (its unit is Ampere) . This differential equation possesses two stable steady solutions[9~10] : $I = 2$ and $I = 0$ (corresponds to active state and passive state , respectively) . In addition ,it has also one unstable steady solution for $I = 1$. However ,due to the effect of the inherent stochastic character , *e. g.* ,presence of thermal noise and the electrode reactions[10~11] , the system will lie necessarily in either the active or the passive state.

## 3 Results and discussion

According to theoretical discussion above ,the stochastic differential equation adopted for this simulation work is

$$dI/dt = (I - 1) - (I - 1)^3 + A\cos(\omega t) + H(t) \cdots \quad (2)$$

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where $I$ is same as that in equation (1) , $A$ refers to the amplitude of the input sinusoid current , $\omega$ *is the angular frequency*. $H(t)$ is input noise (Gaussian white noise) current. In this simulation , after some modifications of the parameters ,the amplitude of sinusoid current and the angular frequency were chosen as $A = 0.38$ and $\omega = 0.002 \times 2\pi$ ,respectively. Consequently ,there is only one variable ,namely the noise amplitude. The angular frequency $\omega$ was chosen to a very low value based on the fact that the relaxation times of typical electrode systems are rather long[12].

The optimum output of the system after modulating the noise amplitude to an optimum value is shown in Fig. 1.

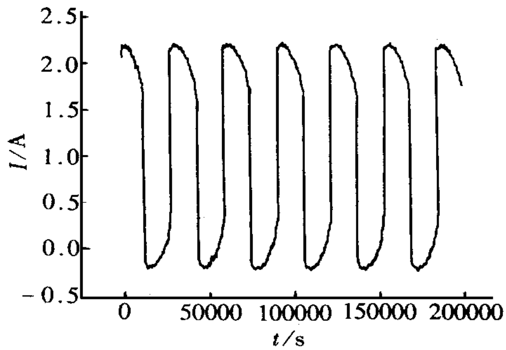


Fig. 1 The optimum output of the system after modulating the noise amplitude to an optimum value

As shown in Fig. 1 ,when the noise amplitude was modified to an optimum value , the state of the system undergoes periodic hopping with respect to every periodic signal. In this circumstance ,the signal gives the system optimal modulation.

In order to further discuss the relationship between the output of the system and the noise amplitude , the notion of SNR was employed. Through the Discrete Fourier Transform operation ,the time series output signal was translated into the frequency domain. Fig. 2 reports the trend of SNR as a function of the noise variance (analogue to noise amplitude) .

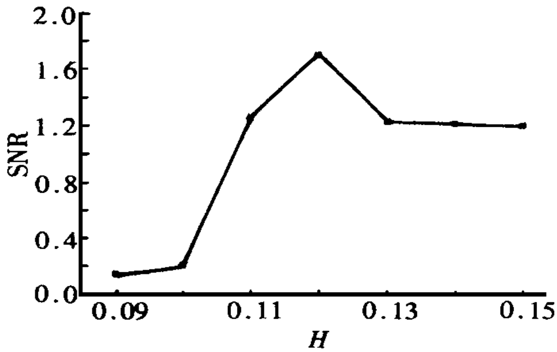


Fig. 2 SNR vs H curve for the output of the system

From Fig. 2 ,it can be seen that there is a maximum for SNR at the corresponding position of the optimum value of noise input . On the left hand of the peak SNR increases with the increment of noise amplitude ,meanwhile on the right hand of the peak ,with the further increment of noise amplitude there's an over output of noise ,SNR hence decreases.

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## 4 conclusion

The appearances of hysteresis loop on the current-voltage curves for the process of active-passive transition of iron rotating disk electrode in 1 mol/L sulfuric acid can be described as a symmetric bistable system. Under this bistable model, the SR phenomenon can be simulated. This work is primary and simple, but may be it can call attentions of the researchers to the SR phenomenon in electrochemistry, and can simulate some people to do further experimental verification.

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# 铁在硫酸溶液中活化-钝化转移过程的随机共振研究

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**摘要**:本文描述了铁在硫酸中活化-钝化转移过程的双稳特征,并模拟出该过程的随机共振现象.

**关键词**:活化-钝化转移,随机共振,双稳态,电化学

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