Theory for EIS Of Quasireversible Charge Transfer In Presence Of Uncompensated Solution Resistance

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Abstract:

We simulate electrochemical impedance spectroscopy (EIS) with applied potential step at a rough electrode forthe quasireversible charge transfer in presence of uncompensated solution resistance. Our phenomenological theory simulate EIS output under influence of potential step on quasireversibility is analyzed for EIS. Detailed model simulation of EIS is performed for a finite fractal roughness. Finite fractal roughness is characterized by its fractal dimension, smallest grain size of roughness and width of the interface. Model predicts the effect of kinetics through a characteristic diffusion-kinetic-ohmic coupling length (L_{Qfi}). The impedance response is therefore interplay of L_{Qfi}, diffusion length (L_D), self similarity index of roughness and the morphological lengths manifesting themselves at different frequencies. Crossover frequencies characteristics of different phenomenological controlled regimes are visible in complex impedance plots. Theory provides helpful insights to understand the influence of kinetics of the system, resistivity of the solution, applied potential and morphological irregularity of the interface on the impedance response.

Keywords: Quasi-reversible charge transfer, Finite fractals, uncompensated solution resistance

1. Introduction

Electrochemical impedance spectroscopy has been in use for several decades for investigatingelectrochemical kinetics. It has been applied in many fields ranging from metal or semiconductor electrode-electrolyte interface, electrode/layer/electrolyte system, porous electrodes,solid electrolytes, fuel cells, membrane assemblies and photovoltaics in general.Information that can be obtained by EIS measurements on the Faradaic process includes both its thermodynamics (standard or formal potentials) and charge as well as mass- transfer kinetics.

In more than a decade long work,Kant and coworkers have established a series of relationship between the observable like current, admittance, absorbance and charge transients with the morphology of the electrodes viapower spectrum of rough interface.[1,2] These include anomalous diffusion reaction rates or diffusion-controlled potentiostatic current transients, anomalous Warburg impedanceat a rough electrode[1,4], solution resistance effect on anomalous Cottrellian current, andanomalous Warburg impedance at a rough electrode, partial diffusion limited interfacialtransfer/reaction at rough electrodeand Gerischer admittance at a rough electrode. These studies connect various phenomena at the interface to the electrode morphology.We wish to explore in this theoretical work, the effect of uncompensated solution resistanceon charge transfer process in the bias dependent impedance response.Figure 1 shows aschematic for the problem underlined at a reconstructed SEM image of disordered electrode.

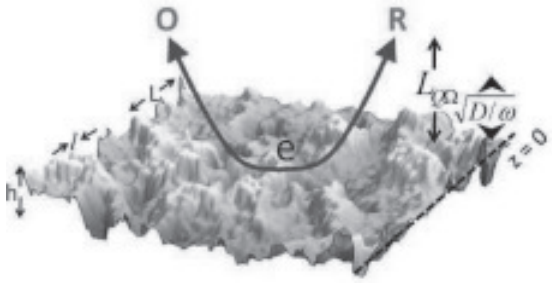


Figure 1:Schematic of bias dependent charge transfer at rough electrode under moderate supporting conditions.

Under the quasi-reversible charge transfer conditions, the current is determined by both mass transfer and charge transfer kinetics. For a single step charge transfer process, at a randomly rough electrode, the diffusion equation can be written as[1]

$$\frac{\partial \delta C_\alpha(\vec{r},t)}{\partial t} = D_\alpha \nabla^2 \delta C_\alpha(\vec{r},t) \qquad (1)$$

For a small AC perturbation signal (ðE(t)), applied to the DC bias potential (E_{DC}) is of the form of E(t) = E_{DC} + ðE(t) [3]

$$L_{Q\Omega}\partial_n \delta C - \delta C = C_*^{DC} + \frac{\theta_{DC}}{(1+\theta_{DC})^2}(C_O^0 + C_R^0) n f \delta E(t) \qquad (2)$$

$$L_{Q\Omega} = L_Q + L_\Omega = \Gamma D(R_{CT} + R_\Omega) \qquad (3)$$

$$\Gamma = \frac{n^2F^2}{RT}\frac{\theta_{DC}}{(1+\theta_{DC})^2}(C_O^0 + C_R^0); R_{CT} = \frac{RT}{nFj_0}(1+\theta_{DC}) \qquad (4)$$

Here, we need to define the concentration field at the electrode/electrolyte interface. This concentration field is the function of boundary profile, therefore we can say that roughness is sensed by the concentration field in an electrochemical measurements. The second order perturbative solution for concentration profile in the Fourier and Laplace transform domain for rough surface can be obtained and hence the current density can also be obtained. Expression for current is obtained from the current density under steady state approximation and hence the admittance can be obtained as

$$Y_p(\omega) = \frac{n^2F^2DA_0}{RT}\frac{\omega_0}{(\omega_0 L_{Q\Omega}+1)}\frac{\theta_{DC}}{(1+\theta_{DC})^2}(C_O^0 + C_R^0) \qquad (6)$$

Planar response has a new phenomenological length scale L_{Qfi}. This contains kineticsas well as the ohmic loss information.The local admittance density expressionfor an arbitraryroughness surface profilecan be represented as sum of various order terms in surface roughness, i.e. upto second order terms.

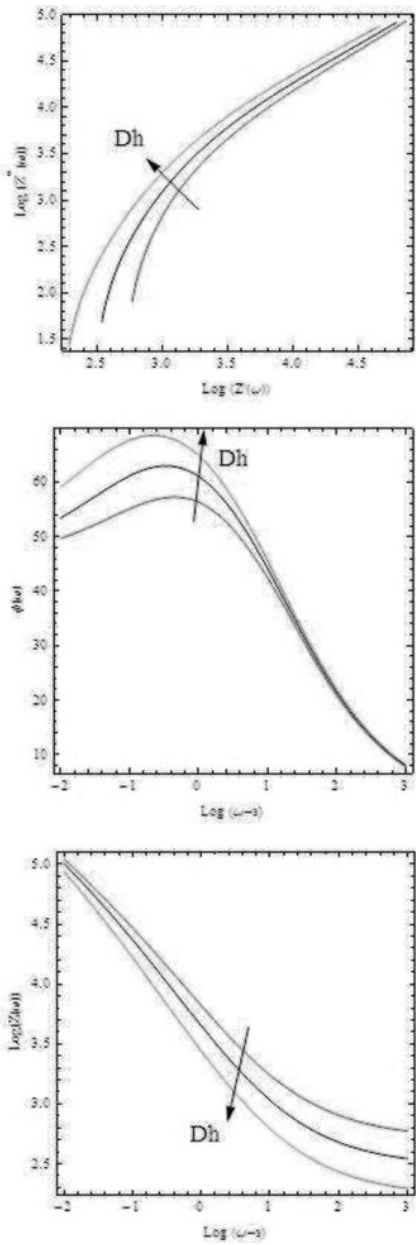
The angular brackets denote an ensemble average over various possible surface configurations. The average admittance is given by [2,4]

$$\langle Y(\omega)\rangle = Y_p(\omega)\left[1 + \frac{\omega_0}{2\pi}\int_0^\infty dK_\parallel\, K_\parallel \left[\frac{\omega_1 - \omega_0}{1+\omega_1 L_{Q\Omega}} + \frac{K_\parallel^2 L_{Q\Omega}}{2(1+\omega_0 L_{Q\Omega})}\right]\langle|\zeta(\vec{K}_\parallel)|^2|\rangle\right]$$

The ensemble averaged admittance expression for a finite self-affine isotropic fractal surface for problem involving sizeable ohmic losses for solution resistance can be obtained by solving resultant integral.The resulting admittance behavior is interplay between the interfacial kinetics, the solution resistance and the roughness features ofthe interface. The total admittance is the summation of smooth surface response and ananomalous excess flux due to fractal roughness.

3. Results and Discussion

Effect of fractal dimension (D_H) on the impedance plot in the presence of some sizeable resistance offered by the electrolyte at an infinite self-affine fractal electrode. The quantity D_H is a direct measure of thesurface irregularity. In the plots, it can be seen that as the fractal dimension increases, the impedance decreases and plateaus off at higher frequencies owing to the overall concentration polarization due to kinetic and ohmic factors. Apparent overall resistance defers the phaseangle shows a crossover to zero towards higher frequency, whereas it tends to have 45^0 towards lower frequency. At intermediate frequency regime, phase angle possesses greater than 45^0. At lower frequencies the plots seem to merge. At intermediate frequencies power law impedance response follows, characteristic of the dynamic response to surface roughness.The slope of the power law region changes with the varying fractal dimension, marking the strong dependence of anomalous response on the fractal dimension (D_H).The Nyquist representation shows that increase in D_H decreases the apparent resistance on the real axis. The higher-frequency effects are resonated in the lower portion of the curve nearthe x-axis where solution resistance has a dominant influence.



Effectof fractal dimension (D_H) on (a) Nyquist plot (b) phase and log of frequency (c) the doublelogarithm plot of impedance. D_H is varied as 2.1; 2.2; 2.3. The plots are generated by using fixed parameters =10 nm, Diffusion coefficient ($D = 5 * 10^{-6}$ cm^2/s) and concentration (CO = CR = 7.5 mM) are used in our calculations, R_{fi}=10 fi cm^2, E_{DC} = 0.01V.

Similarly we have studied the effect of solution resistance (R_{fi}), applied potential (E_{DC}), topothesy length ($l_{ý}$) and lower cut-off length scale on Nyquist plot, phase v/s log of frequency and the doublelogarithm plot of impedance and interpret the results in low, high and intermediate frequency regimes.

4. Conclusions

The analytical relationship between the impedance response under the influence of potential dependent finite charge transfer and solution resistance effects with power spectrum ofroughness has been derived from first principles. The perturbation analysis upto secondorder in roughness profile is obtained for detailed analysis of a stationary random surface.Analysis for finite fractality in roughness is presented in detail. The impedance responseat fractal electrode is affected by the morphological features (signified by fractal dimension(DH), topothesy length; as well as two lateral cut-off lengths in case of finite fractals, i.e. lower cut-off and upper cut-off lengths.

5. Acknowledgement

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6. References

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