Impedance of constant phase element (CPE)-blocked diffusion in film electrodes

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Abstract

We construct a model of ac impedance response to blocked linear diffusion that has a sloped low frequency region in the impedance plot. The approach is based on the transmission line analogy to linear diffusion, and it is equivalent to solving Fick’s law with a boundary condition that allows us to set an arbitrary impedance response at low frequencies. We argue that roughness at the blocking interface gives rise to constant phase element (CPE) response at low frequencies, and we give an impedance model function that can fit data along the whole frequency range when such a CPE is found. This is tested in an experiment of Li⁺ insertion in Nb₂O₅. The model should be of significance for metal oxide thin film electrodes and modified polymer electrodes. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The insertion of cations such as H⁺ and Li⁺ into several oxide host materials in aqueous or non-aqueous solution has been investigated intensively in relation to the technologies of secondary lithium batteries and electrochromic devices. There are at least two important interfaces in an insertion experiment, the contact between the electrode and the electrolyte, which we shall call ‘front contact’ and the ‘back contact’ between the electrode and an electronic conductor. This is sketched in Fig. 1(a).

Electrochemical impedance is one of the best techniques for monitoring some of the changes occurring within intercalation compounds during insertion and extraction. It is widely believed that the kinetics of coloration of metal oxides and the cathode process in secondary lithium batteries is controlled by the diffusion of the inserted species through the electrode [1–5]. The model of Ho et al. [2], has been used to investigate diffusion in myriad experiments of impedance spectroscopy on thin film electrodes. It consists basically in a Randles-type circuit model, represented in Fig. 2, that combines the high frequency resistance of the elec-
trollyte, ionic charge transfer resistance and double layer capacitance at the front contact, and restricted diffusion of the inserted species [6–8]. Because of the following facts, however, the description of diffusion has puzzled researchers for years, and critical information on electrode thickness and transport properties has been obscured. The model of Ho et al. predicts a pure capacitive behavior at low frequencies. This is rarely, if ever, observed, even at very low frequencies. Reported observations on different types of diffusing species and electrode materials show that a certain frequency dispersion can be clearly appreciated in reported measurements of insertion of Li⁺ into Sn oxide [18], and of insertion of H⁺ into vanadium oxide fluorite compounds [13]. The same type of dispersion has been pointed out in relation with the following systems: diffusion of H⁺ into Nb₂O₅ [10], of Li⁺ into TiO₂ [12] and of Li⁺ into Nb₂O₅, into V₂O₅ [14], into TiO₂ [12] and of Li⁺ into vanadium oxide fluorite compounds [13]. The same type of dispersion can be clearly appreciated in reported measurements of insertion of Li⁺ into V₂O₅ [14], into TiO₂ [12], into Li₂V₂O₅ [3], into NiO [17] and into Sn oxide [18], and of insertion of H⁺ into WO₃ [19,20].

Previous attempts to explain the physical origin of the low frequency CPE that appears frequently in thin film electrodes had limited success. Cabanel et al. [10], who stated the problem very clearly, suggested an expression that consists in a straightforward modification of the model of Ho et al. This proposal was presented by the authors as an empirical formula, but it fails to describe correctly the measurements. Very recently Liu and Wu [21] succeeded in showing that the influence of the low frequency CPE in the modeling of diffusion can change the values of the diffusion coefficient by two orders of magnitude, but their treatment is confined to the galvanostatic titration technique. In summary, we lack a theory that rationalizes the normal Warburg diffusive response plus the lower frequency CPE dispersion. It is the aim of this paper to construct a physical model with the common features of blocked finite-length diffusion, but with a CPE instead of a pure capacitive impedance response at low frequencies.

2. The model of Ho et al.

We recall the main features of the model of Ho et al., whose treatment is to be extended. The diffusion impedance is

\[ Z_W(\omega) = R_W \frac{\coth \sqrt{\frac{j\omega}{\omega_0}}}{\sqrt{\frac{j\omega}{\omega_0}}} \]

where \( \omega \) is the circular frequency, \( \omega_0 \) is a characteristic frequency that depends on the species chemical diffusion coefficient \( D \) and the thickness of the film \( L \),

\[ \omega_0 = \frac{D}{L^2} \]

and

\[ R_W = \frac{V_m|dE/dy|}{F S} \frac{L}{D} \]

Here \( V_m \) is the molar volume of the host structure, \( |dE/dy| \) is the slope of the coulometric titration curve, and \( s \) is the surface area of the electrode. It is important to remember how the fact that the current collector is impermeable to M⁺ is incorporated in the model of Ho et al. The diffusive current in response to the small applied ac signal is set to zero in the points of a perfect plane located at the back contact. That is

\[ \frac{\partial(\delta c)}{\partial x} \bigg|_{x=L} = 0 \]

where \( \delta c \) is the excess concentration associated with the ac perturbation. Solving Fick’s equation with Eq. (5) as a boundary condition leads to the classic formula in Eq. (2), thus it seems appropriate to make reference to this classic formula as the impedance of plane-restricted diffusion.

The transmission line of finite length \( L \) in Fig. 1(b) with the terminal impedance \( Z_t \) set to an open circuit \( Z_t = \infty - j\infty \) is a useful analogy of plane-restricted diffusion, which can then be viewed as follows. The injected signal at \( x = 0 \) penetrates the line up to a distance \( \lambda_\omega = L/(\omega/\omega_0)^{1/2} \), after which the capacitors shunt. In the high frequency regime \( \lambda_\omega < L \) and thus semi-infinite diffusion holds, \( Z_W \) being then identical to a Warburg impedance

\[ Z(\omega) = \frac{V_m|dE/dy|}{F S D^{1/2}} \left( j\omega \right)^{-1/2}, \]

which forms a straight line inclined at 45° in the complex impedance plane. At low frequencies \( \omega \ll \omega_0 \) the capacitive response of the volume prevails, because the signal has well reached the end of the line and an equilibrium concentration has been established in the
whole volume of the electrode. In this frequency regime $Z_W$ is effectively the series combination of a resistance $R_w/3$ and a capacitance $C_{LF} = 1/R_w \omega_0$, and accordingly in the complex plane it traces a straight line that intersects the real axis at 90°. These features of $Z_W$ are illustrated in the complex plane plot shown in Fig. 3. The inflection that marks the transition region from low frequency to high frequency behavior is of great significance, because essential information concerning film thickness and transport properties is located there [22]. For any choice of parameters the inflection takes place in a narrow interval of less than one decade of frequency around $f = \omega_0$. This can be visualized in Fig. 3. The main trouble with the plane-restricted diffusion model is that when lines intersecting the real axis of the complex plane at less than 90° are found, which is the most frequent occurrence, the identification of the exact location of the crossover frequency $\omega_0$ becomes impossible as a matter of fact. The only safe route to the determination of the diffusion coefficient is then the value of the Warburg prefactor in Eq. (6), but the quantities $s$ and $|dE/dy|$ introduce additional uncertainties [18,23].

3. CPE-restricted linear diffusion

Our target then is to generalize the plane-restricted diffusion model in order to allow for responses other than the strict vertical line in Fig. 3. To that end, it must be observed that it is Eq. (5) that produces the odd feature of the plane-restricted diffusion model. In effect, the pure capacitive response at low frequencies is a direct consequence of the application of the boundary condition in Eq. (5); this is too stringent a blocking condition for present purposes. To relax it, one simply has to note that the low frequency response of a transmission line such as that in Fig. 1(b) can be changed by offering the signal a path through $Z_t$; this change is formally equivalent to a modification of the boundary condition. The obvious candidate for $Z_t$ is a CPE, so as to accommodate the experimental evidence. But that choice certainly follows from fundamental considerations alone, because in normal circumstances the interface between the thin film and the electronic conductor would be rough, and a vast amount of theoretical [24–26] and experimental [27–30] published work attributes a dispersive CPE impedance response to a blocking interface which is not a perfectly smooth plane but has some roughness and/or porosity. Once we write the pertinent physical constants in the expression of the impedance of the transmission line of Fig. 1(b), which is known,

$$Z(\omega) = \frac{r}{j \omega Z_t} + \frac{r}{j \omega} \coth(L \sqrt{r/j \omega})$$

we arrive at the impedance function of CPE-restricted linear diffusion:

$$Z_{W-CPE}(\omega) = R_w \frac{(j \omega)^n \sqrt{\omega_0}}{j \omega \omega_0 + (j \omega)^n \coth(\sqrt{j \omega/\omega_0})}$$

(8)

In Eq. (8) the constant parameters $\omega_0$ and $R_w$ have the same meaning as in Eqs. (3) and (4); $n$ is the exponent of the low frequency CPE, as in Eq. (1); and $A$ is related to the CPE’s prefactor. Fig. 4 helps the properties of model function $Z_{W-CPE}$ to be visualized. This function should fit impedance data along the whole frequency range where diffusion dominates. One may equally well derive Eq. (8) solving Fick’s equation by the usual Laplace-transform method [31] with an appropriate boundary condition instead of Eq. (5). This will be shown in a future publication.

Now we return to the transmission-line physical picture of diffusion, in order to include the effects of roughness at the back contact not taken into account previously. Going from higher to lower frequencies, at the start, the injected signal does not reach the end of the line, and pure Warburg-like behavior obtains. Therefore $Z_{W-CPE}$ always presents at high frequencies a line inclined at 45° in the complex plane (this implies that if anomalous diffusion occurs, causing a Warburg exponent different from 1/2, a more elaborate model than that presented here should be attempted). When the signal arrives in the back contact, two basic possibilities arise. One is that the interface located there be
Fig. 4. Plots of $Z_{W-CPE}$ in the complex plane for $\omega_0 = 1$ and various values of $n$ and $A$. The inset is a Bode plot of the same function with $\omega_0 = 1$.

less capacitive than the volume, then we find essentially the same situation as in the open circuit case seen previously, and plane-restricted diffusion will be observed even if the back contact is rough. In the opposite case the signal goes through the pits and grooves at the interface and, at frequencies low enough, CPE response is obtained as the frequency is lowered, until the system’s outer cutoff frequency [32,33] is reached. From then on the details of the interface are no longer accessible to the signal, and a pure capacitive response should be expected.

If the interface at the back contact of the electrode is a fractal of dimension $d$, and if the transfer of charge across it is diffusion-limited, then the exponent $n$ of the low frequency CPE in $Z_{W-CPE}$ is determined by the geometry of the interface alone [32,33], according to $n = (d-1)/2$. It must be noted though that in the CPE-restricted diffusion model the low frequency CPE acts on Fick’s law as a boundary condition, and may itself be due to a process other than diffusion, such as the resistive and capacitive properties of the interface at the microscopic scale. Very recent determinations of fractal dimensions in insertion electrodes by Strømme et al. [34] were referred to the front contact.

4. Experimental

Now we examine the results of an experiment conducted to test the $Z_{W-CPE}$ model function. Thin niobium pentoxide films were prepared by a dip-coating technique onto an indium tin oxide electrode by the methodology described elsewhere [35]. The film thickness after one dip determined by scanning electron microscopy was 335 nm. The impedance measurements were performed in a conventional three-electrode cell using a platinum foil as counterelectrode. The dc applied potential was measured using a silver wire quasi-reference electrode immersed in a Li$^+$ ion conducting liquid electrolyte, which was a solution of 0.1 M LiClO$_4$ in propylene carbonate. The thin film working electrode was held at constant voltage 0.75 V by a Princeton Applied Research Model 273 potentiostat. The impedance analyzer was a Solartron model 1260, the signal amplitude was 10 mV r.m.s., and the measurement frequency range was from 5 kHz to 1 mHz. The high frequency part of the recorded data was treated with standard electrochemical impedance software [36] in order to identify the series high frequency resistance, the double layer CPE, and the charge-transfer resistance (Fig. 2), which were then subtracted. The resulting data set, showing a pure Warburg response at high frequencies and a CPE at low frequencies, was fitted to Eq. (8) in the frequency interval from 0.01 to 30 Hz. The results are $R_W = 1196 \Omega$, $\omega_0 = 0.161 \text{ rad s}^{-1}$; $n = 0.701$, and $A = 0.524 \text{ rad}^n \text{s}^{-n}$, and the square of the correlation coefficient is 0.9995. Eq. (3) yields then the value $D = 1.8 \times 10^{-10}$ cm$^2$ s$^{-1}$ for the diffusion coefficient. The goodness of fit is excellent, as can be appreciated in the complex plane plot of Fig. 5.

5. Final remarks and conclusion

A different type of model that also comprises a Warburg-like response followed at lower frequencies by a CPE is a family of impedance functions based on the
approach of de Levie [37], that are used in relation to porous electrodes [38–40]. In that approach the capacitors in the transmission line of Fig. 1 are substituted by a dispersive impedance, which has a physical meaning related to the electrical properties of the interface along the pore’s surface. These models can be distinguished clearly from CPE-restricted diffusion because their Warburg-like part is not a pure Warburg, but has an exponent $\alpha/2$, $\alpha$ being the CPE’s exponent. This is substantially equivalent to the empirical formula of less than one decade of any frequency around $f \approx \omega_0$ suggested by Cabanel et al. [10]. But, on the one hand, if the capacitive behavior at low frequencies is due to the back contact, then there is no general reason why the Warburg and CPE exponents should be proportional, even if anomalous diffusion occurs. And, on the other hand, and leaving aside special cases such as anomalous diffusion, the Warburg exponent 1/2 predicted by both the model of Ho et al. and the CPE-restricted diffusion model (in a certain frequency range beginning approximately at $\omega_0$) is confirmed often by insertion measurements, see the inset in Fig. 5. We have observed this type of pure Warburg response in various spectra, prior to applying the subtraction procedure. We should also like to note that the detailed measurements presented by Cabanel et al. in figure 2 of [10] yield an exponent of 0.49 at high frequency and $n = 0.88$ at low frequency. We may further add that CPE-restricted diffusion must hold for porous electrodes whenever diffusion into the bulk of electrode material grains is the limiting process in a certain interval of frequencies.

For the sake of clarity we have referred the construction of the CPE-restricted diffusion model to the situation represented in Fig. 1 with a compact bulk, a rough back contact, etc. Surely this disposition will be met in many practical instances, but nonetheless with some straightforward modifications the model can describe other specific dispositions and processes. A particularly interesting situation is to have a non-blocking back contact. Assume for instance that the electrode is composed of two different layers, as has been suggested for some systems [41]. Hence, upon arrival in the rough interface between the two layers the diffusing species must experience a blocking that is only partial. In this type of situation a likely model of diffusive transport along the first layer should be a transmission line terminated in a CPE-R parallel combination, and the associated diffusion impedance will be given by Eq. (7), with $Z_1$ replaced by the impedance of the CPE-R parallel combination. A resulting feature of the model is that in the complex impedance plot, one can get a depressed arc in the lowest frequency regime, instead of the constant sloped line shown in Fig. 4.

In conclusion, we have argued that blocking experienced by the ions in insertion experiments is responsible for the observed CPE. Roughness at the back contact is a plausible explanation of its appearance, on the grounds that a CPE impedance is the electrochemical manifestation of a rough interface. We have shown that the proposed generalized impedance function for linear diffusion describes experimental data with very good accuracy. Therefore it is demonstrated that the model allows the relevant physical parameters to be extracted from low frequency impedance measurements.

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