Small-Signal A-C Response Theory for Electrochromic Thin Films

Donald R. Franceschetti*

Department of Physics, Memphis State University, Memphis, Tennessee 38152

and J. Ross Macdonald*

Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27514

The identification and characterization of the processes responsible for the electrochromic properties of thin transition metal oxide films are matters of high current interest. Several authors (1-3) have applied small-signal a-c techniques in this area. Ho *et al.* (2) have analyzed their a-c data on WO_3 with injected Li using the standard Randles (4) equivalent circuit, but with a modified (finite length) Warburg element. Glarum and Marshall (3) have devised a slightly different circuit from their data on IrO_2 with injected protons. Both sets of authors have given some discussion of the theory underlying the use of these circuits. In a somewhat earlier paper (5) the present authors derived an equivalent circuit for an electrochemical system characterized by an electrode adsorption-reaction-diffusion sequence that yields the circuits mentioned above, or parts of them, as limiting cases. Much of this analysis has been recently republished independently by Braunshtein *et al.* (6). In the present paper we discuss our earlier treatment as it might be applied to an electrochromic system. Our treatment leads to an equivalent circuit which, we believe, may be useful in the analysis of impedance or admittance data on electrochromic thin films, particularly if the injection of atoms into the film involves an adsorbed intermediate.

We consider an electrochemical cell consisting of an inert electronic conductor, a thin layer of electrochromic material A_yB, a liquid electrolyte with mobile $A+$ ions, and an electrode of solid A metal, or if A represents hydrogen, a hydrogen electrode. We shall assume that current flow through the system is effectively one-dimensional, at least over the region in which a significant potential drop occurs. We also assume that A_yB is a sufficiently good electronic conductor that the transport of A within the layer of A_yB occurs purely by diffusion.

We assume that the system has been allowed to come to equilibrium under a steady applied potential difference. Then the A_yB layer has a spatially uniform composition and the potential drop falls essentially between the surface of the A_yB layer in contact with the electrolyte and the A electrode. We assume that an $A+$ ion combines with an electron from the conduction band to form an adsorbed intermediate before entering the A_yB film. Adopting the notation of our earlier work (5), we let p_R denote the concentration of the $A+$ ions at the point of closest approach to the A_yB film, let Γ denote the concentration of the adsorbed intermediate, and let b_L denote the concentration of A just inside the surface of the A_yB film. Then for any deviation from the equilibrium potential difference the equations governing the behavior of the reactant species at the A_yB/liquid interface may be written (5, 7)

$$I_{pR} = ev_1\ (p_R, \Gamma, \eta) \qquad [1]$$

$$d\Gamma/dt = v_1\ (p_R, \Gamma, \eta) - v_2\ (\Gamma, b_L) \qquad [2]$$

and

$$J_{bL} = v_2\ (\Gamma, b_L) \qquad [3]$$

where I_{pR} is the faradaic current, J_{bL} is the flux of A into the A_yB layer, v_1 and v_2 are as yet unspecified rate functions, and η is the additional potential drop across the compact layer between the A_yB film and the liquid electrolyte.

Under small-signal a-c conditions we may separate each of the variab es in Eq. [1]-[3] into an equilibrium part and a sinusoidal perturbation, *e.g.*, $p_R = p_{0R} + p_{1R}\exp(i\omega t)$. On making an appropriate Taylor series expansion of the reaction rates about their equilibrium values, we obtain

$$I_{p1R} = e[k_{1f}p_{1R} - k_{1b}\Gamma_1 + (e\eta_1/kT)\gamma_{1f}p_{0R}] \qquad [4]$$

$$i\omega\Gamma_1 = I_{p1R}/e - k_{3f}\Gamma_1 + k_{3b}b_{1L} \qquad [5]$$

and

$$J_{b1L} = k_{3f}\Gamma_1 - k_3 b_{1L} \qquad [6]$$

where each of the k's and γ_{1f} represents a partial derivative of the rate functions v_1 and v_2. We assume that within the A_yB layer the transport of A is governed by Fick's laws, with diffusion constant D_{1e}. In this note we shall assume that the A atoms are completely blocked at the interface between the A_yB layer and the inert electronic conductor, a physically reasonable assumption for the experimental arrangements that have been employed. In this case, the result obtained in Ref. (5) may be written as

$$I_{p1R} = e[k_1{}^*p_{1R} + (e\eta_1/kT)\gamma_1{}^*p_{0R}] \qquad [7]$$

where $k_1{}^* = f_1k_{1f}$ and $\gamma_1{}^* = f_1\gamma_{1f}$, with

$$f_1 \equiv \{1 + k_{1b}/[i\omega + k_{3f}/(1 + F_1(\omega))]\}^{-1} \qquad [8]$$

and

$$F_1(\omega) = \frac{k_{3b}}{\sqrt{i\omega D_{1e}}}\ \mathrm{ctnh}\ (l_e\sqrt{i\omega/D_{1e}}) \qquad [9]$$

where l_e is the thickness of the A_yB film. The quantities $k_1{}^*$ and $\gamma_1{}^*$ may be considered to be complex, frequency-dependent rate constants, a notion first introduced by Lányi (8). If R_c is a constant normalizing resistance, it may readily be shown that $R_cF_1(\omega)$ is the impedance of a length l_e of distributed transmission line of characteristic impedance $R_ck_{3b}/(i\omega D_{1e})^{1/2}$ with series resistance per unit length $R_{ser} \equiv R_ck_{3b}/D_{1e}$ and shunt capacitance per unit length $C_{sh} = i\omega/k_{3b}R_c$, terminated by an infinite resistance.

If the liquid electrolyte employed in the experimental system is fairly concentrated ($>$ 1M) and assuming that the $A+$ ions are appreciably more mobile in the solution than A atoms are in the solid A_yB one may neglect p_{1R} in Eq. [7] and then define an interfacial admittance

$$\check{Y} = \frac{I_{p1R}}{\eta_1} = \frac{e^2p_{0R}}{kT}\gamma_1{}^* \qquad [10]$$

which is represented exactly by the equivalent circuit of Fig. 1. The circuit elements are the charge transfer resistance

$$R_R = kT/(e^2p_{0R}\gamma_{1f}) \qquad [11]$$

the adsorption capacitance

$$C_A = 1/(R_Rk_{1b}) \qquad [12]$$

an adsorption related resistance

$$R_A = R_Rk_{1b}/k_{3f} \qquad [13]$$

and a distributed capacitative element with impedance

* Electrochemical Society Active Member.

Key words: films, impedance, diffusion.

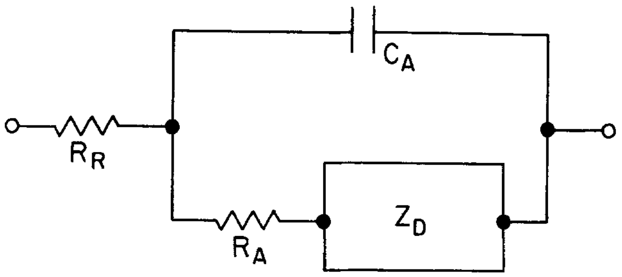


Fig. 1. Equivalent circuit representing the interfacial impedance. See Eq. [10]-[15].

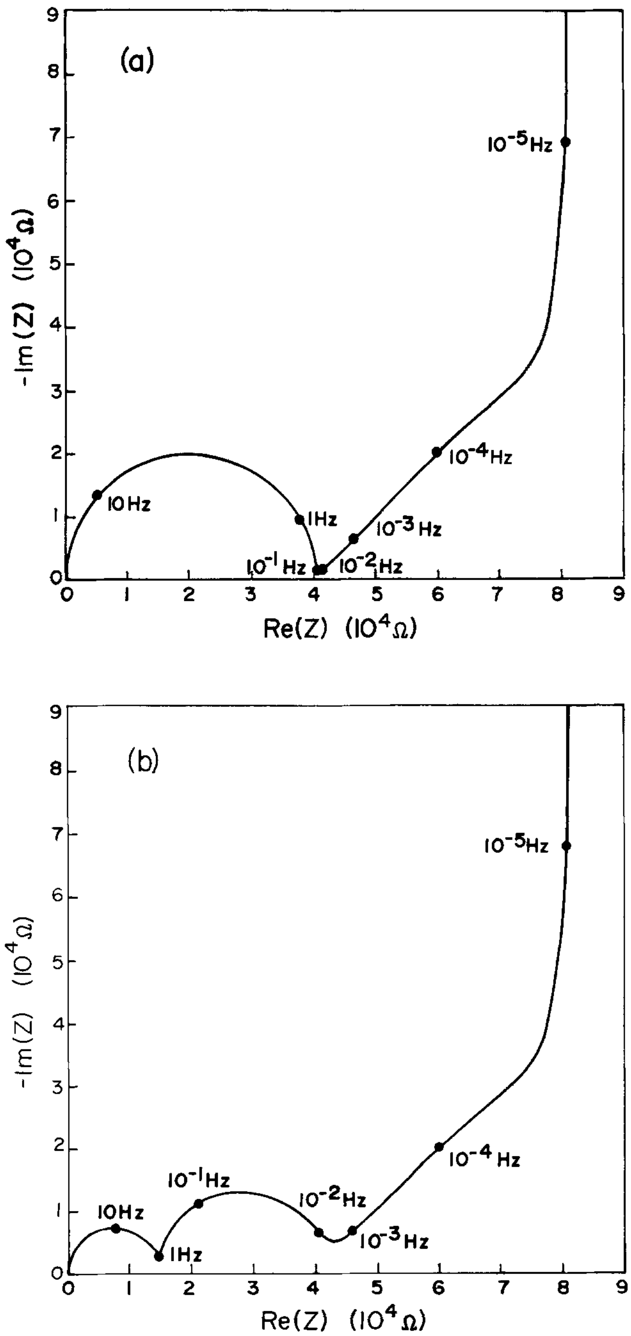
$$Z_D = Z_{Do}\,\mathrm{ctnh}\,(\sqrt{i\omega l_e^2/D_{1e}})/\sqrt{i\omega l_e^2/D_{1e}} \qquad [14]$$

with

$$Z_{Do} = R_R k_{1b} l_e / k_{3f} D_{1e} \qquad [15]$$

When the Warburg element and charge transfer resistance in the Randles circuit (2, 4) are replaced by the circuit segment shown in Fig. 1, one obtains the equivalent circuit appropriate for the system considered in this note.

Some impedance plane plots for this generalized Randles circuit are shown in Fig. 2. In Fig. 2(a) we have set R_A and C_A equal to zero so that our circuit reduces to that of Ho *et al.* (2), consisting of a bulk (liquid electrolyte) resistance R_x, double layer capacitance C_D, charge transfer resistance R_R, and the distributed capacitative element Z_D. The figure shows a single semicircular arc, associated with R_R and C_D, and a straight segment, with 45° slope which curves to approach a vertical asymptote, characteristic of Z_D. In Fig. 2(b) R_A and C_A have been given values so that $R_AC_A >> R_RC_D$, and two semicircular arcs are apparent, the one at lower frequencies being associated with R_A and C_A. In Fig. 2(c), $R_AC_A \approx R_RC_D$ and only a single, approximately semicircular arc is apparent. In fact, the impedance curves of Fig. 2(c) and (a) are almost indistinguishable in shape, even though they represent two distinctly different sets of circuit parameters. We are thus led to suggest that any determination of circuit parameters by graphical analysis of impedance plane curves be confirmed by nonlinear least-squares fitting of the data as a function of frequency to the circuit concerned (9).



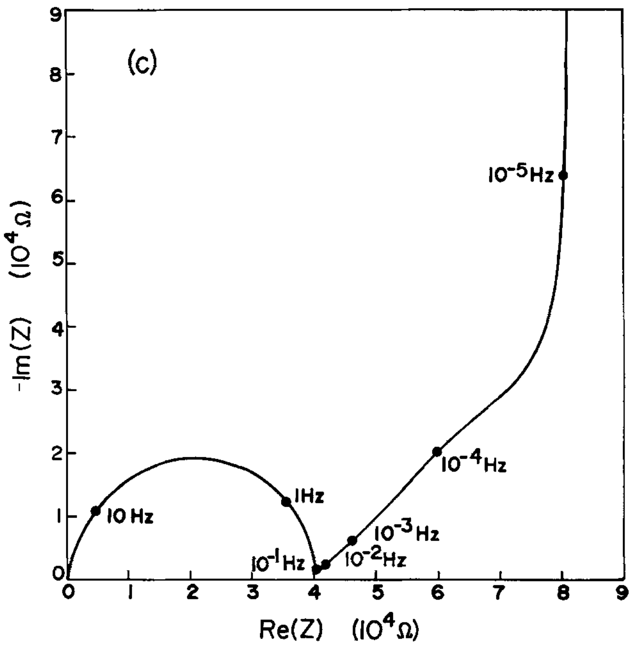


Fig. 2. Impedance plane plots for Randles equivalent circuit with charge transfer resistance and Warburg impedance replaced by circuit of Fig. 1. The bulk resistance, $R_x = 1\Omega$, double layer capacitance, $C_D = 1\ \mu F$, and distributed capacitative element $Z_{Do} = 1000\Omega$, $l_e^2/D_{1e} = 250$ sec, are the same for all plots. (a) $R_R = 40{,}000\Omega$, $C_A = 0$, $R_A = 0$. (b) $R_R = 15{,}000\Omega$, $C_A = 100\ \mu F$, $R_A = 25{,}000\Omega$. (c) $R_R = 15{,}000\Omega$, $C_A = 1\ \mu F$, $R_A = 25{,}000\Omega$.

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