

A comprehensive model for cyclic voltammetric study of intercalation/de-intercalation process incorporating charge transfer, ion transport and thin layer phenomena

M. Noel^{a,*}, V. Rajendran^b

^a Central Electrochemical Research Institute, Karaikudi 630006, India

^b Alagappa Chettiar College of Engineering and Technology, Karaikudi 630004, India

Received 29 September 1999; accepted 17 December 1999

Abstract

A comprehensive model involving intercalation, competitive background reaction and de-intercalation is described. The interaction step is modelled as simple irreversible charge transfer and charge transfer coupled with diffusion. The de-intercalation step is modeled as a thin-film process. Overall cyclic voltammetric (CV) responses under all these limiting conditions are also presented and discussed. The method is also used for comparing typical experimental CV responses reported in the literature. The method is found to be useful in comparing the intercalation processes under different experimental conditions and evaluating model parameters. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Intercalation; De-intercalation; Cyclic voltammetry; Modeling; Thin layer model

1. Introduction

In studies of the electrochemical intercalation of ionic species on graphite [1] and other electrodes in aqueous [2–5] as well as non-aqueous media [6,7], cyclic voltammetry (CV) has been commonly used for a quick estimation of intercalation/de-intercalation efficiency (IDE) under various operating conditions. This trend continues in recent research work in this laboratory [8–11], and elsewhere [12–14]. Some reviews in this area also highlight the use of CV as an important analytical tool along with other methods [15–17].

Despite such extensive use of CV in intercalation/de-intercalation studies, a comprehensive theoretical model applicable for CV has not been available to date. This is mainly due to the involvement of different phenomenological components in the description of this process. The intercalation process itself may be charge-transfer or mass-transport controlled. Invariably, the intercalation pro-

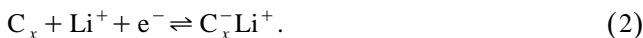
cess occurs along with a competitive parallel process. De-intercalation on the other hand is predominantly a thin-film surface process. Building up the model for such an involved overall process would indeed be interesting and challenging. Recently, Levi and Aurbach [18,19] have achieved an ingenious simplification of the overall process by working at very slow sweep rates in the range of $\mu\text{V s}^{-1}$ [18,19]. Under these conditions, the intercalation as well as the de-intercalation process can be modelled as an overall thin-film process, as was developed earlier [20,21].

The above approach of working at very slow sweep rates or near quasi-equilibrium conditions, however, has its own limitations. Each measurement under these conditions of course involves significantly longer time scales. Apart from this, it is not possible to look at faster time-dependent processes such as charge-transfer kinetics and diffusion. For the calculation of diffusion coefficients of intercalants, for example, it becomes necessary to use other techniques such as AC impedance [22,23]. Hence, it is worthwhile to develop a model on conventional time scales involving charge-transfer, counter-ion transport as well as thin film kinetics. This is the objective of the present work.

* Corresponding author. Tel.: +91-4565-22368; fax: +91-4565-37779.
E-mail address: organic@cscecri.ren.nic.in (M. Noel).

2. Model

Simple reversible anionic or cationic intercalation process on a typical graphite electrode may be represented by Eqs. (1) and (2), respectively, i.e.,



As a general case involving any lattice, L and any monovalent cationic species M^+ , the cationic intercalation process may be represented as follows:



The rate expressions are considered for this overall cationic intercalation process, with the cationic intercalation current as positive. The extension of these expressions for anionic intercalation, however, is obvious and straightforward. The intercalation reaction, Eq. (3), may be determined by the following processes:

- (i) a simple activated irreversible charge-transfer process;
- (ii) a reversible charge-transfer process coupled with the rate of diffusion of cationic species into the lattice space; and
- (iii) an irreversible charge-transfer coupled with the rate of diffusion of intercalant into the lattice.

Apart from the intercalation process at extreme negative potentials, additional cathodic processes such as cation, solvent or impurity reduction and hydrogen evolution may occur. The overall IDE will decrease due to such competitive processes.

The intercalated film can be modelled essentially as a thin film. The de-intercalation process may, thus, be modelled as a thin film process as described by Levi and Aurbach [18,19]. In what follows, the overall voltammetric responses for the intercalation/de-intercalation process involving an intercalation current density i_{in} , a competitive background cathodic current i_b , and a de-intercalation current i_{di} are involved. The intercalation current i_{in} depends on the model described above, i.e., processes (i) to (iii). The overall responses are described below.

2.1. Intercalation rate controlled by charge transfer (case 1)

In this case, the intercalation process is defined by a simple irreversible approximation of the Butler–Volmer, i.e.,

$$i_{in} = i_{ct} = i_{o1} \exp[-nf\alpha n_{a1}(E - E_{th})] \quad (4)$$

In this expression: i_{ct} is the intercalation current density due to charge transfer; i_{o1} is the exchange current density

for the intercalation process; E_{th} is the equilibrium (threshold) potential for intercalation; αn_{a1} is the corresponding transfer coefficient; f is F/RT ; and E is the applied potential.

The competitive background current i_b may be represented by:

$$i_b = i_{o2} \exp[-n\alpha n_{a2}f(E - E_b)] \quad (5)$$

where: i_{o2} and αn_{a2} are the exchange current density and transfer coefficient of the competitive cathodic process, respectively, and E_b is the equilibrium potential of the competitive process.

The relative contribution of the overall charge from these two processes ultimately determines the efficiency of overall intercalation. The IDE may be easily obtained by

$$IDE = q_{in}/(q_{in} + q_b) \quad (6)$$

In this expression, q_{in} and q_b values may be obtained by summing the i_{in} and i_b values at different potentials or time intervals in the voltammetric method using the trapezoidal rule, the charge expressions in accordance with the above rule are:

$$q_{in} = h/2[(i_{in,1} + i_{in,n}) + 2(i_{in,2} + i_{in,3} + \dots + i_{in,(n-1)})] \quad (7)$$

$$q_b = h/2[(i_{b,1} + i_{b,n}) + 2(i_{b,2} + i_{b,3} + \dots + i_{b,(n-1)})] \quad (8)$$

In this expression, the time interval ‘ h ’ for CV is given by Eq. (9), where v = sweep rate and n is the total number of interactions.

$$h = E/n = vt/n \quad (9)$$

The overall cathodic current i_c at any potential is obviously given by:

$$i_c = i_{in} + i_b = i_{ct} + i_b \quad (10)$$

The de-intercalation current for the thin film model is given by:

$$i_{di} = q_{in}(d\theta/dt) \quad (11)$$

where θ is the total mole fraction of intercalation species in the film with an initial value of unity. The $d\theta/dt$ may be described in terms of a charge-transfer rate constant k_s , an equilibrium potential for de-intercalation E_d , (which may or may not be equal to E_{th} , see below), and a lateral interaction parameter g , i.e.,

$$d\theta/dt = -k_s \theta \exp[-\alpha n_{a3}f((E - E_d) + g\theta/2)] + k_s(1 - \theta) \exp[\alpha n_{a3}f((E - E_d) + g\theta/2)] \quad (12)$$

where αn_{a3} is the transfer coefficient for the de-intercalation process.

For the reverse anodic peak, the potential and current are defined by:

$$E = 2vt_m - vt \tag{13}$$

$$i_a = i_b + i_{de}. \tag{14}$$

The effect of intercalation potential E_{th} and the overall voltammetric response are shown in Fig. 1. For a fixed value of background potential E_b , as the difference ($E_{th} - E_b$) increases the intercalation charge, q_{in} , as well as IDE increases (Fig. 1).

For a constant difference in the equilibrium potentials ($E_{th} - E_b$), the relative values of exchange current density of intercalation, i_{o1} , and background exchange current density, i_{o2} , may also have significant influence on the voltammetric response. Obviously, higher values of i_{o1} lead to higher intercalation efficiency.

The de-intercalation potential, E_d , is a very important process parameter. Under ideal conditions, where intercalation/de-intercalation proceeds on a host lattice without any surface transformations, E_{th} must be equal to E_d . In real situations, however, there is a scope to consider the possibility of different de-intercalation potentials. This parameter influences the peak potential alone and not peak current.

The rate constant of the de-intercalation process, k_s , can also influence the de-intercalation peak in similar fashion, as shown in Fig. 2. The de-intercalation peak current value once again remains unaffected (Fig. 2) for slow surface processes.

The lateral interaction parameter, g , can be considered as an overall lump parameter covering the interaction between the intercalated species, as well as lattice transformations and lattice intercalant interactions. This parameter influences the de-intercalation peak current and the half-peak width of the de-intercalation peak (Fig. 3).

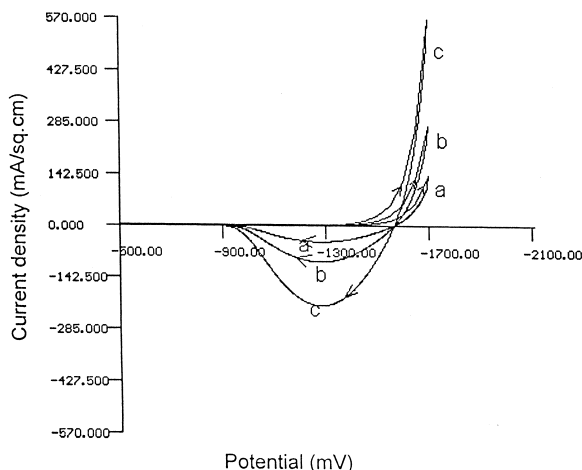


Fig. 1. Theoretical CV for intercalation/de-intercalation process; Influence of ($E_{th} - E_b$): ($E_{th} - E_b$) = (a) 100 mV, (b) 150 mV, (c) 200 mV.

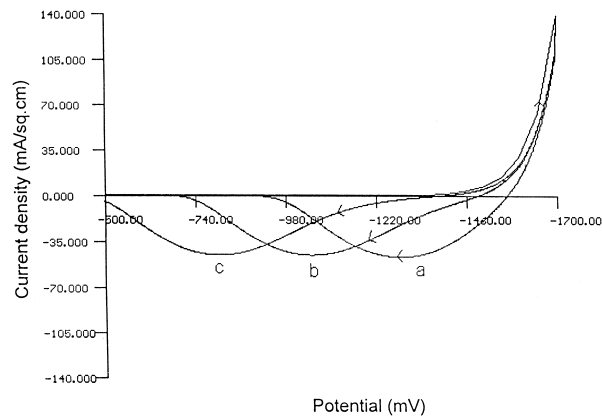


Fig. 2. Theoretical CV for intercalation/de-intercalation process. Influence of k_s : (a) $k_s = 0.1$, (b) $k_s = 0.01$, (c) $k_s = 0.001$.

2.2. Intercalation rate controlled by reversible charge-transfer and diffusion (case 2)

Under the operating conditions of intercalated battery systems over extended periods, the overall rate of intercalation ultimately depends on the rate at which the intercalants diffuse into the host lattice. In most cases, even under practical CV time scales, the diffusion can become the rate-controlling process. The two stages of the generalized intercalation reaction 3 may be represented as electron-transfer (step 3a) followed by diffusion of cationic intercalant into the lattice (step 3b), where L and L⁻ represent neutral and charge lattice sites.



The electron-transfer coupled with diffusion process is quite similar to the solution phase electron-transfer/diffusion problem treated earlier [24], but with one significant difference. The concentration gradient is now on the electrode side of the electrode–electrolyte interface rather than

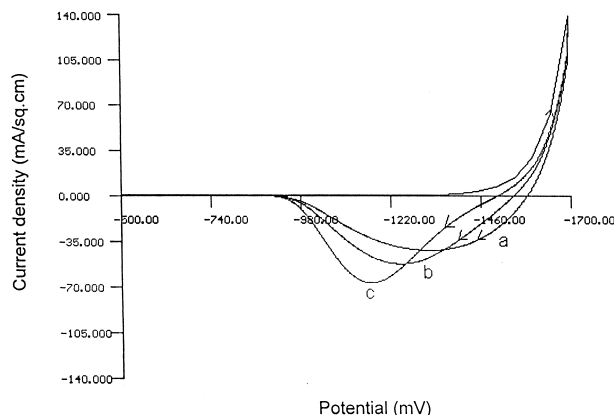


Fig. 3. Theoretical CV for intercalation/de-intercalation process. Influence of g : (a) $g = -5$, (b) $g = -3$, (c) $g = -1$.

on the solution side. This problem is also similar to the electrodeposition of metals like cadmium on a mercury electrode under semi-infinite linear diffusion conditions. The concentration gradient in this process during the anodic dissolution step occurs in the interfacial layer of the mercury film in contact with the electrolyte solution. In the intercalation/de-intercalation process, however, the concentration gradient during intercalation as well as de-intercalation steps occurs at the electrode surface region.

Despite these differences, mathematically, the model for all these processes, which involve electron transfer coupled with semi-infinite linear diffusion, is the same. Hence, the overall diffusion-limited current expression developed earlier [24] can also be employed here. The overall intercalation current, i_{in} , for a reversible charge-transfer coupled with diffusion ($i_{r,d}$) is given by [24]:

$$i_{in} = i_{r,d} = nFA C_o \sqrt{Dnfv\pi} \chi(at). \quad (15)$$

In this expression, C_o refers to the initial bulk concentration of the intercalant whose diffusion towards the lattice sites (L^-) controls the limiting rate. The above expression was originally developed for diffusion of electroactive species in a solution whose concentration is very low (mM). With intercalation processes, the intercalant concentration in the solution is significantly higher and, thus, diffusion of counter ions into the host lattice from the interphase is the rate-determining step. For this phenomena, the same rate expressions can be employed. For example, this procedure is adopted in describing the CV behaviour of metal ion deposition and subsequent dissolution from a hanging mercury drop electrode [24].

In this equation, the current function $\chi(at)$ can be expressed as an infinite series solution as proposed by Nicholson and Shain [24], i.e.,

$$\sqrt{\pi}\chi(at) = \sum_{j=1}^{\infty} (-1)^{j+1} \sqrt{j} \exp[-jnf(E - E_{th})]. \quad (16)$$

In a recent work by one of the authors [25], the procedure for summing up this series by the Pade approximation method using continued fraction has been described in detail [25]. The Pade coefficients for [10/11] $p_1, p_2 \dots p_{10}$ and $q_1, q_2 \dots q_{11}$ are presented in Table 1. Using

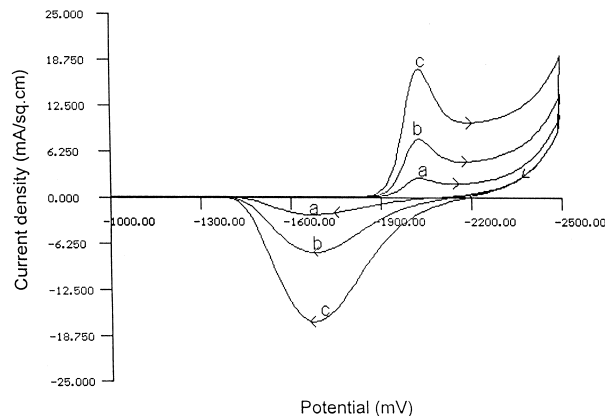


Fig. 4. Theoretical CV for intercalation/de-intercalation process (reversible charge transfer coupled with diffusion). Influence of D : (a) $D = 10^{-7}$, (b) $D = 10^{-6}$, (c) $D = 5 \times 10^{-5}$.

these coefficients, the function $\chi(at)$ can be calculated from the Pade expression:

$$\chi(at) = \frac{p_1 x + p_2 x^2 + \dots}{q_1 x + q_2 x^2 + q_3 x^3 \dots}, \quad (17)$$

where $x = (E - E_{th})n$.

The calculation of the overall current potential response is once again quite similar to the procedure described in Section 2.1, where the current expression for the intercalation in Eq. (4) is replaced by new current expression for i_{in} (Eq. 15).

Apart from the parameters that influence i_b and i_{di} , the overall CV response in this case may be influenced by E_{th} , the diffusion coefficient of intercalant in the host lattice and the sweep rate. Typical CV responses showing the effect of the diffusion coefficient are presented in Fig. 4. The intercalation and de-intercalation peak current and peak potential values are significantly influenced by the diffusion-coefficient and sweep rate.

2.3. Intercalation rate controlled by irreversible charge-transfer and diffusion (case 3)

The expression for the intercalation current [24], i_{in} , for irreversible charge-transfer coupled with diffusion is given by Eq. (18). Based on arguments similar to those proposed in Section 2.2, this expression can be employed for calcu-

Table 1

Pade's coefficients for calculating $\chi(at)$ involving reversible charge-transfer coupled with diffusion (case 2)

i	1	2	3	4	5	6	7	8	9	10	11
p_i	-136.3	-239.5	114.9	138.6	-145.1	56.7	217.9	94.7	11.6	0.25	-
q_i	-136.3	-432.3	-260.3	246.7	94.8	-124.3	-255.1	429.4	195.6	30.4	1.0

Table 2

Pade's coefficients for calculating $\chi(bt)$ involving irreversible charge-transfer coupled with diffusion (case 3)

i	1	2	3	4	5	6	7	8	9	10	11
p_i	2829.6	2274.2	864.0	-91.5	-91.5	36.4	55.8	21.19	4.1	0.026	-
q_i	1596.4	4112.7	4230.7	1940.0	121.7	-192.0	30.6	100.6	49.5	11.0	1.00

lating the counter ionic diffusion coupled with irreversible charge-transfer in to the host lattice.

$$i_{in} = i_{r,d} = nFAC_o\sqrt{\alpha_{na1}Dfv\pi}\chi(bt), \quad (18)$$

$$\text{where: } \sqrt{\pi}\chi(bt) = \sum_{j=1}^{\infty} (-1)^{j+1} \sqrt{\pi}/\sqrt{(j-1)!} \\ \times \exp\left[-jn\alpha_{na1}f\left((E - E_{th}) + (1/\alpha_{na1})\ln(\sqrt{\pi db}/k_h)\right)\right]. \quad (19)$$

$$\text{In this expression: } b = \alpha_{na1}nfv; \quad v = \text{sweep rate.} \quad (20)$$

The current function $\chi(bt)$ can be calculated using the analytical expression, which is identical to Eq. (17), for which p_i and q_i values are given in Table 2 and x is given by Eq. (21), i.e.,

$$x = \alpha_{na1}\left[E - E_{th} + (RT/\alpha_{na1}F)\log(\sqrt{\pi D_0 b}/k_h)\right]. \quad (21)$$

The calculation of overall current-potential response is once again quite similar to the procedure described in Section 2.1, where the expression for intercalation, namely, Eq. (4), is replaced by the new current expression, Eq. (18).

Typical CV showing the effect of the heterogeneous rate constant on the overall response are shown in Fig. 5. This parameter is found to influence both intercalation and de-intercalation peaks significantly (Fig. 5). When the intercalation process occurs quite close to the background process (for the lower overall heterogeneous rate constant)

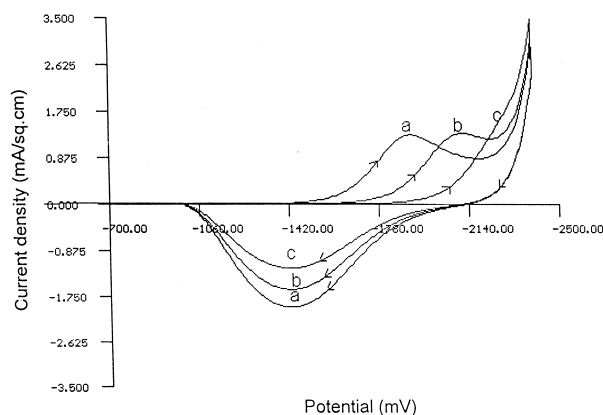


Fig. 5. Theoretical CV for intercalation/de-intercalation process (irreversible charge-transfer coupled with diffusion). Influence of k_h : (a) $k_h = 0.001$, (b) $k_h = 0.0001$, (c) $k_h = 0.00001$.

the intercalation peak current appears to be higher. This is purely due, however, to a merger of the background current along with the intercalation current.

Quite interestingly, even slight changes in the transfer coefficient values can influence significantly the overall voltammetric response (Fig. 6). The overall IDE can also vary accordingly. The sweep rate can also influence the voltammetric response. At higher sweep rates, the intercalation charge decreases. By contrast, the overall IDE increases with sweep rate.

3. Comparison with experimental responses and evaluation of model parameters

A number of systems show CV responses, which correspond to simple irreversible charge-transfer control. Typical CV responses for fluoride ion intercalation on a graphite surface are shown in Fig. 7 [8]. The model parameters evaluated from closely similar theoretical voltammograms are also presented for comparison.

Experimental voltammetric responses for fluoride ion intercalation in aqueous (Fig. 7a) and aqueous methanolic media (Fig. 7b) are quite similar. The IDE, however, is shown experimentally to be higher in aqueous methanolic media. The voltammetric simulation data (see caption of Fig. 7) clearly indicates that the exchange current density for the background oxidation process, i_{o2} , is considerably lower in aqueous methanolic media. The i_{o1}/i_{o2} value is

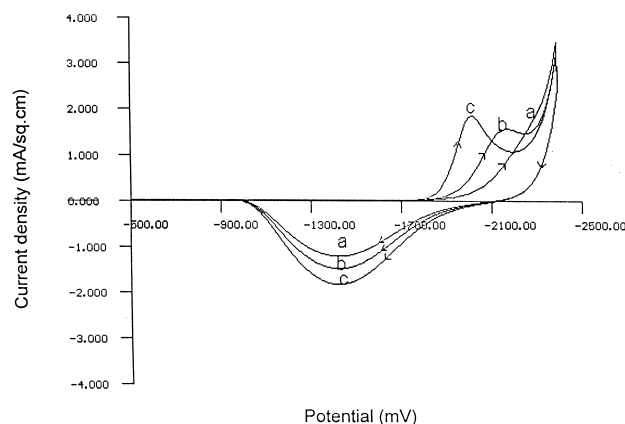


Fig. 6. Theoretical CV for intercalation/de-intercalation process (irreversible charge-transfer coupled with diffusion). Influence of α_{na2} : (a) $\alpha_{na2} = 0.3$, (b) $\alpha_{na2} = 0.4$, (c) $\alpha_{na2} = 0.6$.

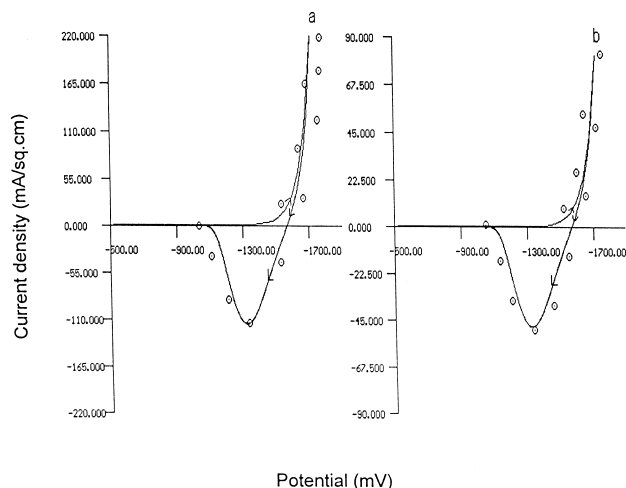


Fig. 7. Experimental (o) and theoretical (–) CV for a HPC electrode in 10 M HF: (a) aqueous solution ($i_{o1} = 0.012$ mA, $i_{o2} = 0.01$ mA, $E_{th} = 1100$ mV, $E_b = 1200$ mV, $k_s = 0.1$, $v = 40$ mV, $\alpha_{na1} = 0.4$, $g = -2$); (b) aqueous methanolic (50 vol.%) solution ($i_{o1} = 0.005$ mA, $i_{o2} = 0.001$ mA, $E_{th} = 1100$ mV, $E_b = 1200$ mV, $k_s = 0.1$, $v = 40$ mV, $\alpha_{na1} = 0.4$, $g = -2$).

close to unity in aqueous media, but is 5 in aqueous methanolic media. This lower background current essentially leads to higher efficiency in aqueous methanolic media.

The classical study of anion intercalation by Beck et al. [2] seems to follow the model of reversible charge-transfer coupled with diffusion rate. Typical experimental results are compared with the models voltammograms in Fig. 8. In strong acidic media, the anionic intercalation process proceeds much faster with considerably higher exchange current densities. The intercalation rate is significantly higher than the diffusion rate and background oxidation rate. The threshold potential for ClO_4^- and BF_4^- intercalations also appear to be identical. The small differences in

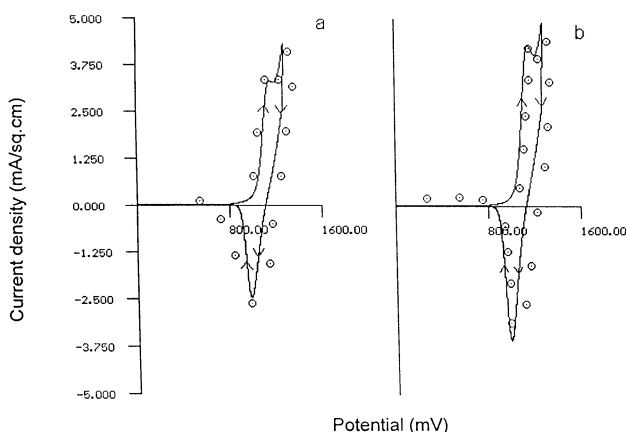


Fig. 8. Experimental (o) and theoretical (–) CV for intercalation/de-intercalation process with CPP ($v = 1$ mV/s): (a) 4 M HClO (62%) ($E_{th} = 1120$ mV, $E_b = 1120$ mV, $v = 1.0$ mV, $D = 0.000005$, $l_0 = 0.5$, $k_s = 0.01$); (b) 5 M HBF (50%) ($E_{th} = 1120$ mV, $E_b = 1120$ mV, $v = 1.0$ mV, $D = 0.000005$, $l_0 = 0.5$, $k_s = 0.01$), $\alpha_{na1} = \alpha_{na2} = \alpha_{na3} = 0.4$.

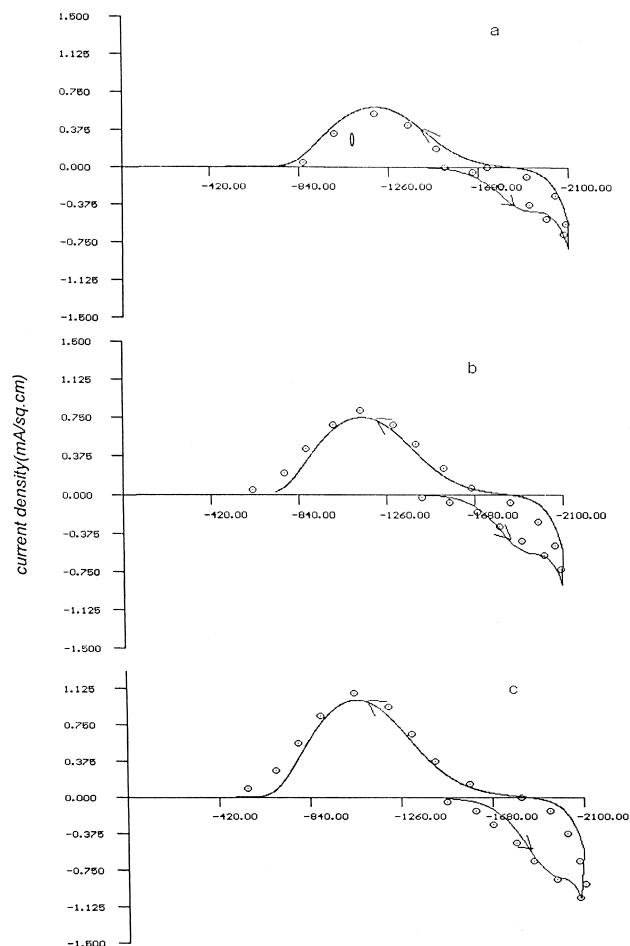


Fig. 9. Experimental (o) and theoretical (–) CV of HOPG in 0.05 M Mg Cl₂-DMSO solution ($E_{th} = -1200$ mV, $E_b = -1500$ mV, $i_{o2} = 0.00005$ mA, $k_s = 0.01$, $k_h = 0.000001$, $D_0 = 0.00005$, $\alpha_{na1} = \alpha_{na2} = \alpha_{na3} = 0.4$). (a) $v = 5$ mV/s, (b) $v = 8.33$ mV/s, (c) $v = 16.66$ mV/s.

the voltammetric responses are due to slight changes in the diffusion coefficients of the intercalants in the graphite lattice.

Cationic intercalation studies by Maeda and Touzain [12] can be cited as an example involving irreversible charge-transfer coupled with diffusion (Fig. 9). In this case, both the cathodic and anodic peak potentials shift considerably with sweep rate. This shows that the charge-transfer rate of intercalation (i_{o1}) and de-intercalation (k_s) control the overall process in addition to the diffusion coefficient. It is also expected that the intercalation of a bivalent cation like Mg^{2+} with its solvation shell would indeed be quite difficult and, hence, rate controlling.

4. Conclusions

A simple model involving intercalation, the competitive background process and the de-intercalation process is presented in this work. The computation procedure for the overall voltammetric response for this process has also

been developed. This has become possible specifically because of the availability of simple analytical expressions for the current functions, which involve diffusion processes [25]. The model is also found to be useful in evaluating the process parameters by comparing these with the experimental voltammetric response. This procedure can be easily employed for studying a wide range of intercalation processes using one of the simplest and routine electroanalytical techniques, CV. Further extension of this model to cover multiple stages of intercalation/de-intercalation is also possible. There is, of course, considerable scope for further work in this direction.

Acknowledgements

The authors acknowledge The Director, Central Electrochemical Research Institute, Karaikudi, INDIA, for his kind permission to publish this paper.

References

- [1] J. Simonet, *J. Electroanal. Chem.* 75 (1971) 719.
- [2] F. Beck, H. Junge, H. Krohn, *Electrochim. Acta* 26 (1981) 799.
- [3] F. Beck, H. Krohn, W. Kaiser, *J. Appl. Electrochem.* 12 (1982) 505.
- [4] F. Beck, H. Krohn, *Synth. Met.* 14 (1986) 137.
- [5] Y. Maeda, Y. Okemoto, M. Inagaki, *J. Electrochem. Soc.* 132 (1985) 2370.
- [6] J.O. Besenhard, H.D. Fritz, *Electroanal. Chem. Interfacial Electrochem.* 53 (1974) 329.
- [7] J.O. Besenhard, E. Theodoridou, H. Mohwald, J.J. Nickl, *Synth. Met.* 4 (1982) 211.
- [8] M. Noel, R. Santhanam, M. Francisca Flora, *J. Power Sources* 56 (1995) 125.
- [9] R. Santhanam, M. Noel, *J. Power Sources* 56 (1995) 101.
- [10] R. Santhanam, M. Noel, *J. Power Sources* 63 (1996) 1.
- [11] R. Santhanam, M. Noel, *J. Power Sources* 66 (1997) 47.
- [12] Y. Maeda, P.H. Touzain, *Electrochim. Acta* 33 (1988) 1493.
- [13] Y. Maeda, *Synth. Met.* 24 (1988) 267.
- [14] Y. Maeda, S. Harada, *Synth. Met.* 31 (1989) 389.
- [15] S. Flandrois, *Synth. Met.* 4 (1982) 255.
- [16] J.O. Besenhard, in: W. Muller-Warmuth, R. Schollhorn (Eds.), *Progress in Intercalation Research*, Kluwer Academic Publishing, London, 1994, p. 457.
- [17] R. Santhanam, M. Noel, *J. Power Sources* (1997) in press.
- [18] M.D. Levi, D. Aurbach, *J. Electroanal. Chem.* 421 (1997) 79.
- [19] M.D. Levi, D. Aurbach, *J. Phys. Chem. B* 101 (1997) 4630.
- [20] H. Angerstein-Kozlowski, J. Klinger, B.E. Conway, *J. Electroanal. Chem.* 75 (1977) 45.
- [21] E. Laviron, *J. Electroanal. Chem.* 101 (1979) 19.
- [22] M.D. Levi, D. Aurbach, *J. Phys. Chem. B* 101 (1997) 4641.
- [23] N. Takami, A. Saton, M. Hara, T. Ohsaki, *J. Electrochem. Soc.* 142 (1995).
- [24] R.S. Nicholson, I. Shain, *Anal. Chem.* 36 (1964) 706.
- [25] V. Rajendran, PhD Dissertation, Alagappa University, Karaikudi, India (1998).