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Mass transport and kinetic aspects of thionyl chloride reduction at the platinum microelectrode

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Abstract

The mass transport and electrochemical kinetic characteristics during the electrochemical reduction of thionyl chloride were investigated using a platinum microdisk electrode. Diffusion coefficients and standard rate constants were determined from fast scan cyclic voltammetric, chronoamperometric, and pulse voltammetric measurements. Activation energies of the diffusion process, as well as the electron transfer process, have also been determined. The results indicate that in 0.5 M LiAlCl₄/SOCl₂ solutions the activation energies are much higher than those obtained at higher concentrations. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lithium/thionyl chloride batteries have been used for a number of applications in astronaut equipment [1,2] and biomedical devices [3,4]. Despite much progress in design and optimization of these batteries, our fundamental knowledge of SOCl₂ reduction is poor. The reduction of thionyl chloride has been investigated extensively [5–10], but the detailed mechanism is still a subject of debate. Film formation at the cathode during the reduction of thionyl chloride has been suggested, based on the diffusion coefficients found [8,9]. Chiu et al. [8] estimated the values of diffusion coefficients ranging from 10⁻¹⁰ to 10⁻¹² cm² s⁻¹ for the 3.0 M LiAlCl₄/SOCl₂ system, while Choi et al. reported that the diffusion coefficients were in the range of 10⁻⁹–10⁻¹¹ cm² s⁻¹ for the 1.5 M LiAlCl₄/SOCl₂ system. The discrepancy between the reported values has been noted, but comprehensive studies have not been reported.

The object of the present paper is to systematically investigate the effects of reaction time, LiAlCl₄ concentration and temperature on the dynamics of film formation processes during the electroreduction of thionyl chloride using microelectrode techniques.

2. Experimental

Thionyl chloride from Merck Company (GR grade) was redistilled using the same method as Venkatesetty [11], with 150 ml additions of triphenyl phosphite to 750 ml of thionyl chloride. LiAlCl₄ (Anderson, battery grade) was dried under vacuum and was stored in a VAC glove box prior to use. A single compartment glass cell was used in this study. Fast scan cyclic voltammetric, chronoamperometric, and pulse voltammetric measurements [12] were performed using a PC-controlled potentiostat (BAS 100B). These techniques, performing experiments on different time scales, allowed us to examine the dynamic characteristics of film formation processes on the electrode.

3. Results and discussion

Fig. 1 shows cyclic voltammograms of Pt, in 0.5 M LiAlCl₄/SOCl₂, taken at a freshly prepared electrode and taken after five cyclic voltammetric cycles. The electrochemical process is irreversible as evidenced by the lack of both a reversal current (Fig. 1a) and the symmetric peaks (Fig. 1b). Peak I decreases steadily with each cycle for the slow scan rate cases, but remains essentially constant with each cycle for the fast scan rate cases.

This behavior can be attributed to the accumulation of reaction products on the platinum surface and a continuous

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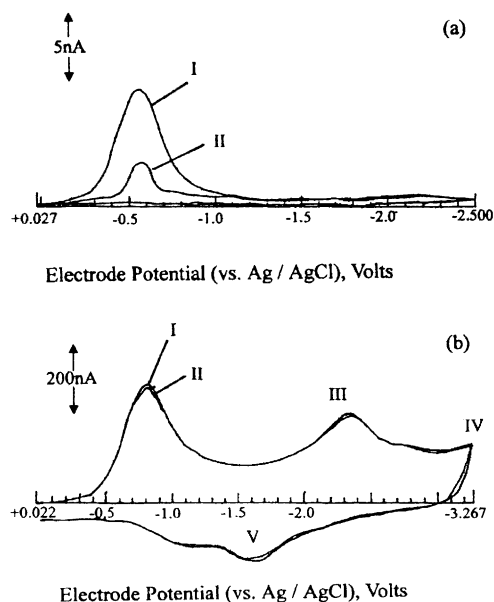


Fig. 1. Cyclic voltammograms of Pt in 0.5 M LiAlCl₄/SOCl₂: (a) sweep rate 100 mV/s; (b) sweep rate 102 V/s.

thickening of the product layer with each cycle. To obtain more information on this reacting system, cyclic voltammetric experiments at a fresh platinum microdisk electrode were carried out using different scan rates. The typical cyclic voltammograms recorded are shown in Fig. 2.

The peak potentials shifted to negative potentials at faster scan rates. This behavior indicates a slow electron transfer. Pletcher [13] has indicated that for a microelectrode running at fast scan rates, the traditional equations developed by Randles, Nicholson and Shain can be adopted. For a totally irreversible reaction, the peak current (I_p in ampere) is given

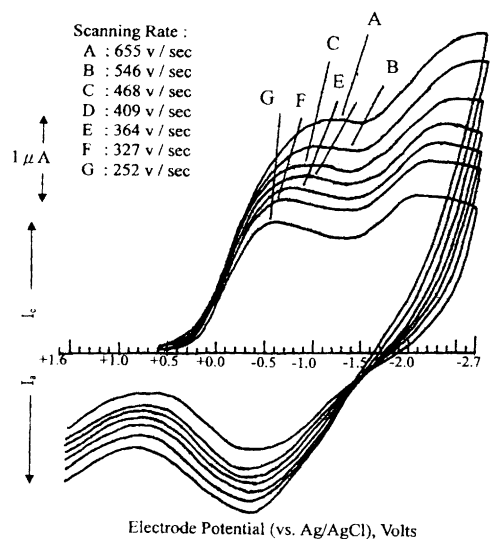


Fig. 2. Cyclic voltammograms recorded at a platinum microdisk electrode in SOCl₂ containing 0.5 M LiAlCl₄ at 25°C.

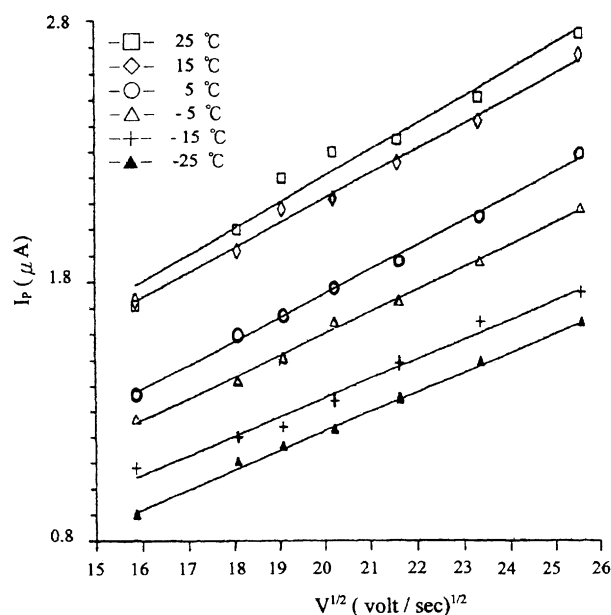


Fig. 3. I_p vs. $v^{1/2}$ plots obtained from the cyclic voltammograms in 1.8 M LiAlCl₄/SOCl₂ solutions at different temperatures.

by the following equation [14]:

$$I_p = (2.99 \times 10^5) n(\alpha n_a)^{1/2} A C_0^* D_0^{1/2} v^{1/2} + \text{correction term} \quad (1)$$

The peak currents are plotted against the square root of scan rates in Fig. 3.

It is discernible from Fig. 3 that the peak current versus $v^{1/2}$ curves do follow the relationship as given in Eq. (1). Similar behavior has been observed in 0.5 and 1.0 M LiAlCl₄/SOCl₂ solutions. The peak potential corresponding to Eq. (1) is [14]

$$E_p = \text{constant} - \frac{RT}{2\alpha n_a F} \ln v \quad (2)$$

A plot of E_p versus $\ln v$ determined at different temperatures is presented in Fig. 4. The graph exhibits a linear correlation between the peak potential and the $\ln v$. The parameter αn_a can then be determined from the slope. The αn_a value obtained can be used to evaluate the diffusion coefficient according to Eq. (1), deduced from the slope of I_p versus $v^{1/2}$ curve.

The diffusion coefficients obtained from these plots are listed in Table 1. These data show an increase in diffusion coefficient with increasing LiAlCl₄ concentration and with increasing temperature. The temperature and concentration effects on conductivity of LiAlCl₄/SOCl₂ electrolyte have been studied by Fey [15], which showed that below 298 K, conductivity increased with increasing temperature, and that maximum conductivity occurred in 1.8 M solutions at all temperatures. Dependence of both the diffusion coefficient and conductivity on LiAlCl₄ concentration as well as temperature followed the same pattern. Our diffusion coefficient

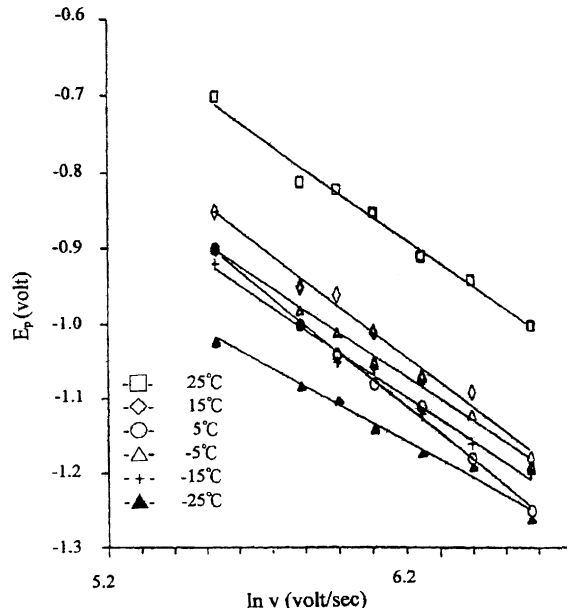


Fig. 4. Relationship between E_p and $\ln v$ for Pt in 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ at different temperatures.

results are consistent with other studies [8,9], but much lower than those observed in liquid phases. This observation again leads to the conjecture that porous solid films may have formed during the electrochemical reduction of thionyl chloride.

We also investigated the effect of reaction time on the value of the diffusion coefficient determined by other electrochemical experiments — chronoamperometric and pulse voltammetric measurements.

In pulse voltammetric experiments, we always scanned the potential repeatedly (scan rate 50 mV s^{-1} ; scan range -1.5 to $+1.0 \text{ V}$) until essentially reproducible current versus potential curves were obtained (usually after six scans). Thereafter, we performed the pulse experiments (pulse width 1 s; pulse period 8 s). The response of current to the potential step at a microdisk is given by [13]

$$I = 4nFD_0C_0^*r_0 + \frac{nF\pi^{1/2}D_0^{1/2}C_0^*r_0^2}{t^{1/2}} \quad (3)$$

The typical diffusion coefficients determined are shown in Fig. 5. In order to get a deeper insight into the reduction

Table 1
Diffusion coefficients determined by cyclic voltammetry

T (K)	Diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$)		
	0.5 M	1.0 M	1.8 M
298	5.22×10^{-9}	5.48×10^{-9}	6.16×10^{-9}
288	4.04×10^{-9}	5.15×10^{-9}	5.86×10^{-9}
278	3.60×10^{-9}	4.83×10^{-9}	5.30×10^{-9}
268	2.96×10^{-9}	4.24×10^{-9}	4.49×10^{-9}
258	0.70×10^{-9}	1.50×10^{-9}	3.83×10^{-9}
248	0.35×10^{-9}	1.47×10^{-9}	3.24×10^{-9}

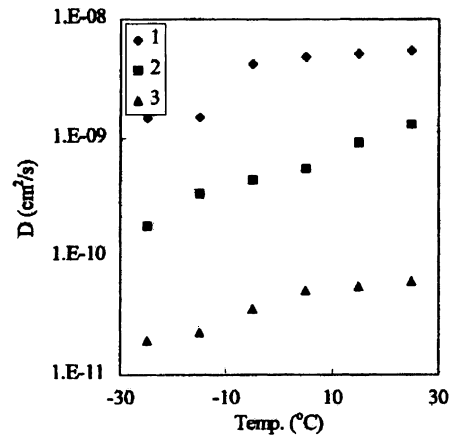


Fig. 5. Variation of diffusion coefficient with temperature as measured by: (1) fast scan cyclic voltammetry; (2) chronoamperometry; (3) pulse voltammetry. Solution: 1.0 M $\text{LiAlCl}_4/\text{SOCl}_2$.

process in $\text{LiAlCl}_4/\text{SOCl}_2$ solutions as a function of the films grown, a series of chronoamperometric measurements were performed under pretreatments identical to those used in the pulse voltammetric study. The steady-state current response to the potential step is given by [13]

$$I = 4nFD_0C_0^*r_0 \quad (4)$$

Though a steady-state was usually reached within a few seconds, we always took data (steady-state current) at 100 s after the potential step applied. The diffusion coefficient was then determined using Eq. (4). Diffusion coefficients measured using this technique compared with those obtained using fast scan cyclic voltammetry and pulse voltammetry are shown in Fig. 5. The typical reaction time of each cyclic voltammetric, pulse voltammetric, and chronoamperometric measurement are, respectively, a few milliseconds, 100 odd seconds, and 200 odd seconds. When the reduction reaction is activated, the film thickness seemed to increase with respect to the reaction time. Hence, Fig. 5 provides better evidence of the growth of film with increasing reaction time. It can be concluded that the film-forming theory correctly accounts for the diffusion coefficient reduction results shown in Fig. 5.

To explore the nature of the film formed, we adopted the classical Arrhenius plot to determine the apparent activation energies of the diffusion through porous film process, based on the diffusion coefficients determined experimentally. The results are presented in Table 2.

Table 2
Activation energy of the diffusion process

LiAlCl_4 concentration (M)	Activation energy (kJ mol^{-1})	
	By cyclic voltammetry	By chronoamperometry
0.5	12.80	26.05
1.0	8.76	15.88
1.8	8.29	13.27

Table 3
Standard rate constant determined from cyclic voltammetric measurements

T (°C)	Standard rate constant (cm s ⁻¹)		
	0.5 M	1.0 M	1.8 M
25	7.42×10^{-4}	7.49×10^{-4}	7.87×10^{-4}
15	6.06×10^{-4}	6.15×10^{-4}	7.62×10^{-4}
5	4.87×10^{-4}	5.59×10^{-4}	5.33×10^{-4}
-5	2.17×10^{-4}	2.42×10^{-4}	3.25×10^{-4}
-15	1.08×10^{-4}	1.94×10^{-4}	3.02×10^{-4}
-25	0.51×10^{-4}	0.79×10^{-4}	0.99×10^{-4}

The apparent activation energies determined from the cyclic voltammetric experiments are lower than those in the corresponding chronoamperometric cases. This is consistent with results shown in Fig. 5. It should also be noted that the activation energy depends on the concentration of LiAlCl₄ as well. The activation energy was higher at the lower concentration of LiAlCl₄, indicating much compact film was formed in a lower concentration case.

For an irreversible reaction, an expression for I_p in terms of E_p is given by the following equation [14]:

$$I_p = 0.227nF(\pi r_0^2)C_0^*k^0 \exp\left[-\frac{\alpha n_a F}{RT}(E_p - E^0)\right] \quad (5)$$

The standard heterogeneous rate constant k^0 can then be determined from the above equation, based on data from cyclic voltammetric measurements performing at high scan rates. Table 3 presents the measured k^0 's. The standard rate constants showed a slight increase with increasing LiAlCl₄ concentration and a strong increase with increasing temperature. The activation energies calculated from the Arrhenius plots are 34.54, 27.64 and 24.25 kJ mol⁻¹ for 0.5, 1.0 and 1.8 M LiAlCl₄ cases, respectively. Choi et al. [9] have indicated that the standard rate constant varies from 10⁻¹¹ cm s⁻¹ at a passivated surface to 10⁻⁶ cm s⁻¹ at a fresh surface. Our standard rate constants are higher than those obtained by Choi et al. [9] by a few orders of magnitude, but we believe that our results are more consistent with the values observed at a fresh electrode surface.

4. Conclusion

The mass transport and electron transfer characteristics of thionyl chloride reduction have been investigated using fast scan cyclic voltammetric, chronoamperometric, and pulse voltammetric techniques. Diffusion coefficients are in the range of 10⁻¹¹–10⁻⁹ cm² s⁻¹, depending on the reaction time, concentration of LiAlCl₄, and temperature. The results obtained support the conjecture that a porous film formed on the Pt electrode surface during the electrochemical reduction of thionyl chloride. The standard rate constants range from 10⁻⁵ to 10⁻⁴ cm s⁻¹ at a nearly fresh electrode surface, depending on the LiAlCl₄ concentration and the temperature. We also conclude from this study that it is important to run the battery at a high LiAlCl₄ concentration because 0.5 M LiAlCl₄ shows higher activation energy and a lower diffusion coefficient.

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