



Electrochemical studies of ferrocene in a lithium ion conducting organic carbonate electrolyte

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ARTICLE INFO

Article history:

Received 2 June 2009

Accepted 17 June 2009

Available online 25 June 2009

Keywords:

Ferrocene oxidation
Non-aqueous electrolyte
Rotating disk electrode
Diffusion coefficient
Kinetics
Voltammetry
Lithium-ion battery

ABSTRACT

We carried out a detailed study of the kinetics of oxidation of ferrocene (Fc) to ferrocenium ion (Fc⁺) in the non-aqueous lithium ion conducting electrolyte composed of a solution of 1 M LiPF₆ in 1:1 EC:EMC solvent mixture. This study using cyclic (CV) and rotating disk electrode (RDE) voltammetry showed that the Fc⁰/Fc⁺ redox couple is reversible in this highly concentrated electrolyte. The ferrocene and ferrocenium ion diffusion coefficients (*D*) were calculated from these results. In addition, the electron transfer rate constant (*k*⁰) and the exchange current density for the oxidation of ferrocene were determined. A comparison of the kinetic data obtained from the two electrochemical techniques appears to show that the data from the RDE experiments are more reliable because they are collected under strict mass transport control. A Tafel slope of c.a. 79 mV/decade and a transfer coefficient α of 0.3 obtained from analysis of the RDE data for ferrocene oxidation suggest that the structure of the activated complex is closer to that of the oxidized specie due to strong interactions with the carbonate solvents. The experiments reported here are relevant to the study of redox reagents for the chemical overcharge protection of Li-ion batteries.

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1. Introduction

Interest in non-aqueous solvents for electrochemical research and practical applications such as lithium batteries has increased significantly over the past four decades. Ferrocene is a useful reference material for non-aqueous electrochemistry as it demonstrates good solubility, invariant redox potentials and excellent chemical and electrochemical reversibility in organic electrolytes [1]. The reversibility of the (Fc⁰/Fc⁺) redox couple was established from polarographic studies [2] soon after the discovery of this organo-iron compound in 1951 by Kealy and Pauson [3]. Previous studies [4] of the electrochemistry of ferrocene in various non-aqueous solvents revealed a reversible one-electron process. The diffusion coefficient (*D*) of ferrocene in different solvents was found to be inversely dependent on the viscosity of the solvent medium. Weaver and co-workers [5] conducted a study of the thermodynamic effects of solvent dynamics on various metallocene redox couples by both theoretical and experimental methods. Their results indicated that solvent viscosity contributed to the high-energy barrier, which influenced the kinetics of outer-sphere reactions. Mass transfer of the electroactive species to the electrode surface is a major factor in the rate of an electrochemical

oxidation or reduction reaction. If the electron transfer step is not hindered kinetically, movement of the electroactive species through the solution becomes the rate-limiting step in this case. As a result, electrochemical measurements are frequently used to determine diffusion coefficients of electroactive species and kinetics of electrode reactions. The process of diffusion is important in a wide variety of chemical scenarios, including kinetics of rapid reactions, chromatographic and electrophoretic separations, and battery electrode reactions. A literature review [6–10] revealed some prior studies of ferrocene electrochemistry in propylene carbonate (PC) solutions containing lithium salts. In the first of these studies, Abraham and Alamgir [10] investigated the electrochemical properties of Fc in a polyacrylonitrile-based gel polymer electrolyte (PAN)-EC/PC-LiClO₄ and established that the oxidation of ferrocene is electrochemically reversible. They found that the diffusion coefficient of Fc decreased by an order of magnitude in the gel polymer electrolyte compared with liquid electrolytes having similar Li salt concentrations. To the best of our knowledge, few studies concentrating on ferrocene oxidation kinetics in highly concentrated solutions of Li salts in organic carbonates of the types used in Li-ion batteries have been performed. Such studies are relevant in view of the fact that ferrocene and its derivatives have been shown to be potentially useful redox reagents for the chemical overcharge protection of rechargeable lithium and lithium-ion (Li-ion) batteries [11–15]. In this application, ferrocene added to the electrolyte in a rechargeable Li or Li-ion battery cell is oxidized at a potential

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slightly positive of the oxidation potential of the positive electrode in the cell and the ferrocenium ions thus produced diffuse to its negative electrode and gets reduced to regenerate ferrocene. Consequently, the electrode potential remains locked at the oxidation potential of ferrocene and prevents the cell from overcharge. This type of chemical shuttles for overcharge protection is highly desirable to protect individual cells in a battery having two or more cells connected in series from overcharge during recharge with the result of improving cell performance and mitigating safety hazards. In this work, we investigated ferrocene redox chemistry in 1 M LiPF₆/1:1 EC:EMC which is a typical liquid electrolyte used in Li-ion batteries. Another motivation for our study is that these ferrocene experiments can serve as models for investigating the redox chemistry of other chemical shuttle reagents used for overcharge protection of rechargeable Li-ion batteries [16–19]. We report the mass transport and kinetic parameters of the Fc⁰/Fc⁺ couple in this prototypical Li-ion battery electrolyte. The results of this study should further our ability to design and develop redox shuttles in non-aqueous electrolytes leading to improved performance and safety in Li-ion and Li-air batteries [20]. A comparison of the results obtained from CV and RDE experiments is useful in understanding the role of mass transport on the kinetic parameters of redox reagents for Li-ion batteries.

2. Experimental

2.1. Chemical reagents

All reagents were of electrochemical grade unless stated otherwise. Battery grade solvents, ethylene carbonate (EC) and ethyl methyl carbonate (EMC) and lithium hexafluorophosphate (LiPF₆) (battery grade, >99.9%, H₂O < 20 ppm) were obtained from Ferro Corporation, Cleveland, Ohio. Ferrocene was purchased from Sigma–Aldrich, Allentown, PA.

2.2. Instrumentation

The electrochemical experiments were performed with a VoltaLab (Radiometer Analytical Inc., model-VoltaLab 10) potentiostat in an airtight electrochemical cell. The electrochemical cell designed and built in-house consisted of a traditional 3-electrode system utilizing Li/Li⁺ as the reference electrode and platinum wire as the counter electrode. A glassy carbon working electrode (3 mm diameter) was employed for the cyclic voltammetry experiments. The electrodes were polished with 0.5 mm and 0.05 mm alumina paste prior to the experiments. For RDE experiments, the glassy carbon electrode was rotated with an Autolab RDE rotor. Scan rate analyses were performed using 3.3 mM solutions of ferrocene in a 1 M LiPF₆/1:1 (by volume) EC:EMC electrolyte, and scan rates were varied between 5 mV/s and 300 mV/s. All of the cyclic voltammetry experiments were initially performed in an Ar-atmosphere glove box where H₂O and O₂ concentrations were kept below 5 ppm and temperature was held at 22 ± 2 °C. RDE experiments were conducted outside the glove box in a glove bag purged with argon. The conductivities of the solutions were measured using a 4-electrode conductivity cell with a Thermo Scientific Orion Model 550A Multiparameter Meter.

Electrolyte viscosities were measured with a size 1 Ubbelohde Viscometer. Measurements and calibration were performed according to ASTM protocol as described by the manufacturer. Efflux time between the upper and lower fiducial marks on the apparatus were monitored with a stopwatch. Average times for four runs were recorded, with all results averaged together. The viscosities were measured at room temperature, 22 ± 2 °C.

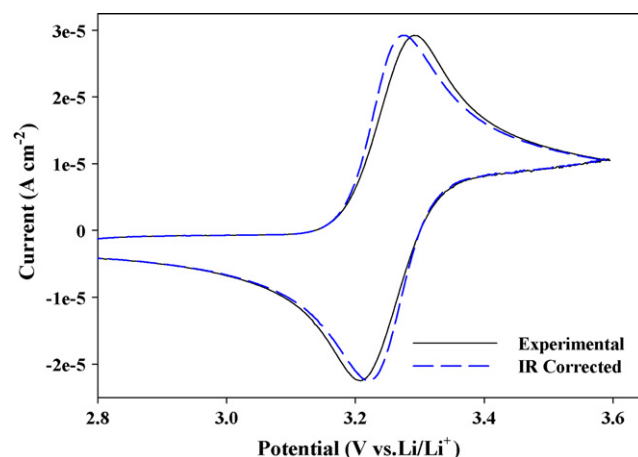


Fig. 1. Cyclic voltammograms for the oxidation of 3.3 mM Ferrocene in 1 M LiPF₆/1:1 EC:EMC on a glassy carbon working electrode at a scan rate of 100 mV s⁻¹.

3. Results and discussion

3.1. Cyclic voltammetry

The redox chemistry of ferrocene was studied using cyclic and rotating disk voltammetric techniques and the results are compared. The electrolyte solution used for these studies was characterized by determining its conductivity and dynamic viscosity with values of 8.8 mS/cm and 4.66 cP, respectively at room temperature. Fig. 1 shows the cyclic voltammograms (CVs) of the ferrocene redox couple on a glassy carbon (GC) electrode in 1 M LiPF₆/1:1 EC:EMC solution (hereafter referred to also as the carbonate electrolyte) at a sweep rate of 100 mV s⁻¹. Our study was restricted to glassy carbon electrodes, since surface adsorption effects on platinum electrodes are well documented [21]. Also, glassy carbon electrodes are practically more relevant to Li-ion batteries as one or another form of carbon is present in the electrodes of the battery. At low concentrations, ferrocene oxidation in many organic electrolyte solutions does not precipitate surface films on glassy carbon electrodes and, thus, would serve as a good standard for non-aqueous electrochemistry. The CV data were corrected for Ohmic (iR) losses using the well-established semi-integral technique [22] (see Fig. 1). Equilibrium is established quickly between the active species as the voltammetric responses of ferrocene appear between 3.22 V and 3.28 V vs. Li/Li⁺. The peak potential separation ΔE_p between the anodic and cathodic peak potentials ranged from 60 mV to 67 mV with an average of 63 ± 0.002 mV. These values are close to the theoretical value of 59 mV for a one-electron reaction. For a reversible process the peak width is given by the following relationship.

$$E_{p/2} - E_p = 2.2 \left(\frac{RT}{nF} \right) \quad (1)$$

Where $E_{p/2}$ is the half-peak potential at the half value of the peak current, E_p , is the peak potential, F is the Faraday constant and n is the number of electrons in the reaction. From the data obtained at the sweep rate of 5 mV/s, the number of electrons n was calculated to be 1.05 (see Table 1). Analysis of the CVs over the whole sweep ranges (see Table 1) gave n values close to this indicating that the number of electrons transferred in the reaction is one. We found the electrochemical charge ratio (Q_c/Q_a) determined from the area under the oxidation (i_{pa}) and reduction (i_{pc}) peaks to be over 91%.

Cyclic voltammetry is a useful technique for discerning kinetics, rates, and mechanisms in addition to thermodynamic parameters. The magnitude of the current, I , in a cyclic voltammogram is a function of temperature, concentration, C_{analyte} , electrode area, A , the number of electrons transferred, n , the diffusion coefficient, D ,

Table 1
Voltammetric properties of Fc⁰/Fc⁺.

Scan rate (V) mV/s	$E_{pa} \pm 0.002$ V	$E_{pc} \pm 0.002$ V	ΔE_p	Charge ratio, Q_c/Q_a	Number of e^- , n
5	3.283	3.224	0.059	0.92	1.051
10	3.283	3.224	0.059	0.95	1.053
25	3.282	3.223	0.064	0.93	1.053
50	3.280	3.222	0.065	0.92	1.050
75	3.281	3.220	0.067	0.89	1.092
100	3.287	3.221	0.06	0.91	1.176
200	3.279	3.216	0.063	0.92	1.125
300	3.280	3.221	0.063	0.91	1.045

and the speed at which the potential is scanned, ν , related by the Randles–Sevcik equation (Eq. (2)).

$$I_{pa} = (2.69 \times 10^5)n^{3/2}AD^{1/2}\nu^{1/2}C \quad (2)$$

Fig. 2A shows both the cathodic and anodic peak potential variations with sweep rates. The dependence of I_{pa} on sweep rate is evident at both low and high scan rates. The little variation in both the reduction and oxidation peak positions with increase in sweep rates reflects the reversibility of the system. The Randles–Sevcik plot (Fig. 2B) shows a linear relationship between I_p vs. $\nu^{1/2}$ passing through the origin. Assuming $n = 1$ we calculated the theoretical Randles–Sevcik plots, which agree with the experimental data. This infers that ferrocene is a reversible redox couple in this media and follows Scheme 1.

The voltammetric parameters for 3.3 mM Fc in the carbonate electrolyte are summarized in Table 1. All potential values are reported vs. the Li/Li⁺ reference electrode. From the

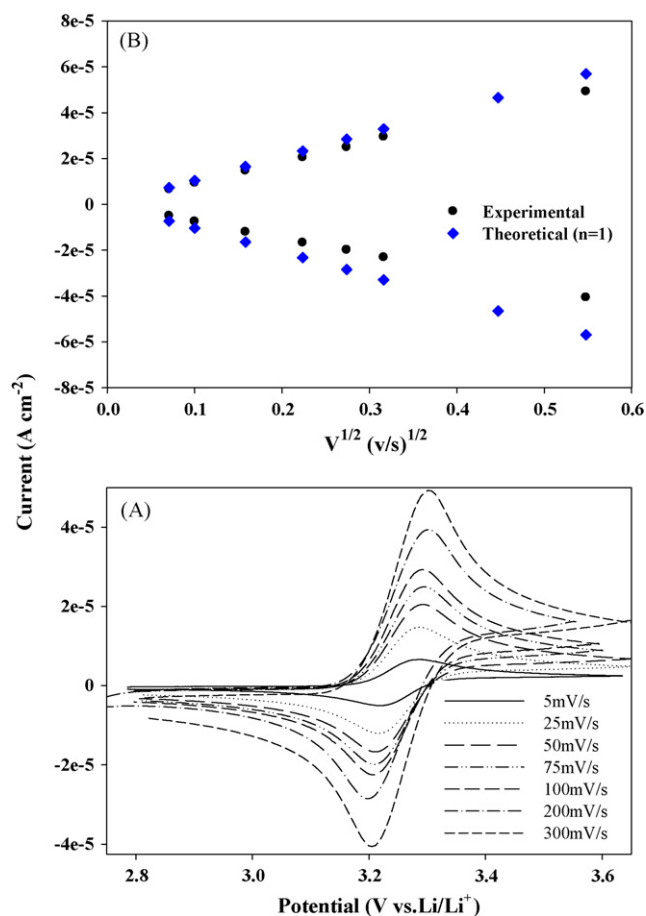


Fig. 2. (A) Cyclic voltammograms for Fc/Fc⁺ in 1 M LiPF₆/1:1 EC:EMC on a GC electrode at sweep rates between 5 mV s⁻¹ and 300 mV s⁻¹. (B) Randles–Sevcik plot of peak current vs. square root of the scan rate for the curves in (A).

dependence of current on scan rate, the diffusion coefficients of ferrocene and ferrocenium ion in solution were calculated as $2.03 \times 10^{-6} \pm 0.2 \text{ cm}^2 \text{ s}^{-1}$ and $1.38 \times 10^{-6} \pm 0.1 \text{ cm}^2 \text{ s}^{-1}$, respectively. The lower diffusion coefficient of ferrocenium ion is understood as arising from interactions between the ferrocenium cation and the PF₆⁻ anion as well as solvent molecules. The diffusion coefficient of ferrocene we found is an order of magnitude lower than that reported for PC/0.1 M LiClO₄ [6]. The lower value obtained in the present work is attributed to higher viscosity of the concentrated solution. This points out the importance of the present work.

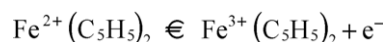
The diffusion coefficient of a species in solution is inversely proportional to the viscosity of the solution according to Walden's Rule. The theoretical diffusion coefficient of this system can be determined by the relationship between diffusion coefficient and solution viscosity given by the Stokes Einstein equation (Eq. (3)).

$$D = \frac{kT}{6\pi\eta a} \quad (3)$$

In this equation k is the Boltzmann constant, T is temperature, η is dynamic viscosity and a is the effective hydrodynamic radius of ferrocene. The hydrodynamic radius is influenced by a number of factors such as solubility of analyte, solvent molecule size and polarity of the solvents. In this case we decided to use the crystallographic radius of ferrocene (0.32 nm) [23]. The dynamic viscosity (4.65 cP) was calculated from the solution's kinematic viscosity ($0.0372 \text{ cm}^2 \text{ s}^{-1}$) and density (1.25 g cm^{-3}) we measured. The theoretical diffusion coefficient is $D = 1.50 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, very close to the measured value.

3.2. Rotating disk electrode

Rotating disk electrode is a hydrodynamic electrode technique which utilizes convection as the mode of mass transport as opposed to CV which is governed by diffusion. Convection is more efficient and is not diffusion limited with the result that the analytical data is more reproducible and precise. Thus a comparison of the kinetic parameters obtained from CV and RDE experiments is informative to elucidate the role of mass transport on electrode reaction kinetics. Fig. 3A shows RDE voltammograms for ferrocene at a series of rotation rates. It is evident from the data that the current generated by the RDE method is much larger than that generated under diffusion control (Fig. 1A). The much larger current obtained using RDE reflects the efficiency of this method. Also notice that there is significant increase in anodic current (i.e. Fc⁰ to Fc⁺) while the amount of cathodic current (i.e. Fc⁺ to Fc⁰) is negligible, essentially making the cyclic voltammogram anodic. This is due to the vast difference in concentration between the Fc⁺ and Fc⁰. The bulk solution contains Fc, which provides a constant supply to the rotating electrode while the concentration of Fc⁺ ions at the electrode is so



Scheme 1.

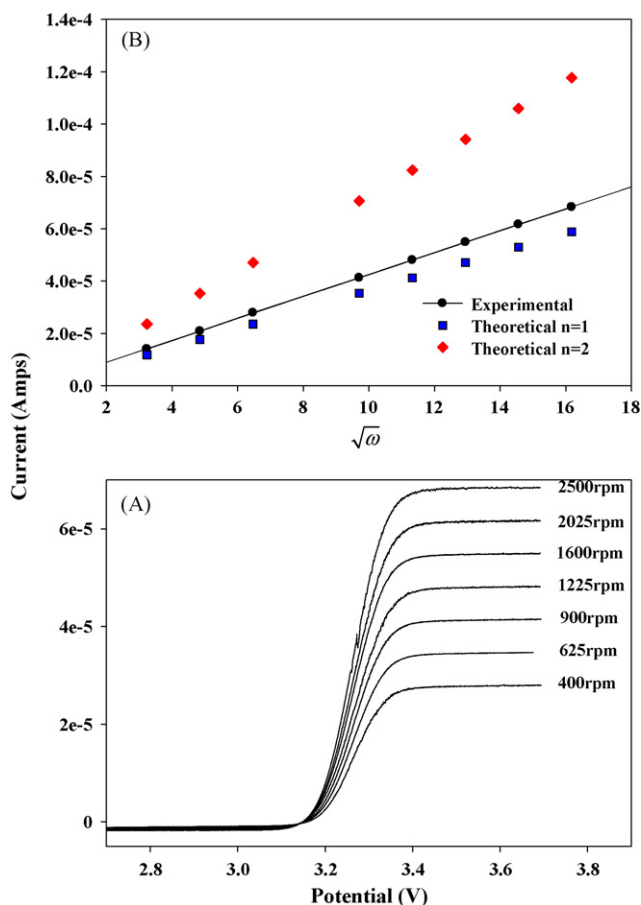


Fig. 3. (A) Disk currents on a RDE obtained in 1 M LiPF₆/1:1 EC:EMC in the anodic sweep at room temperature by various rotation rates. (B) Levich plot of limiting current vs. square root of rotation for the data in (A) at scan rate = 10 mV s⁻¹.

minuscule that little anodic current is produced. The Levich equation (Eq. (4)) establishes relationship between current at the RDE and concentration of the analyte.

$$I_{\text{lim}} = (0.620)nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C, \quad (4)$$

where I_{lim} is the limiting current density (A cm⁻²), n is the number of electrons for the reaction, F is the Faraday constant (96,500 C mol⁻¹), D is the diffusion coefficient of ferrocene in the solution, ν is the experimentally determined kinematic viscosity of the solution (0.0372 cm² s⁻¹), C is the concentration of ferrocene in the solution (3.3 mM) and ω is the angular frequency ($2\pi f/60$). Furthermore, the Levich equation allows us to construct a plot of I_{lim} vs. $\omega^{1/2}$ to determine a value of D which was found to be $2.35 \times 10^{-6} \pm 0.2 \text{ cm}^2 \text{ s}^{-1}$. This value is slightly higher than determined from the aforementioned CV experiments. The RDE data also give insight into the number of electrons transferred in the electrochemical reaction by comparing the limiting currents to the rotation rate of the electrode. These Levich plots, shown in Fig. 3B, display well defined linear plots indicating a simple mass transfer controlled electrode process. The slope of the Levich plot for the experimental data closely parallels the theoretical line for a one-electron reaction ($n=1$). We can apply the Tafel equation (Eq. (5)) which relates the rate of an electrochemical reaction to the overpotential, according to

$$\log i = \log i_0 + \left(\frac{1 - \alpha n F}{RT} \right) \eta \quad (5)$$

In this equation η is overpotential for the anodic reaction and the other symbols have their usual meaning. The Tafel plot is corrected

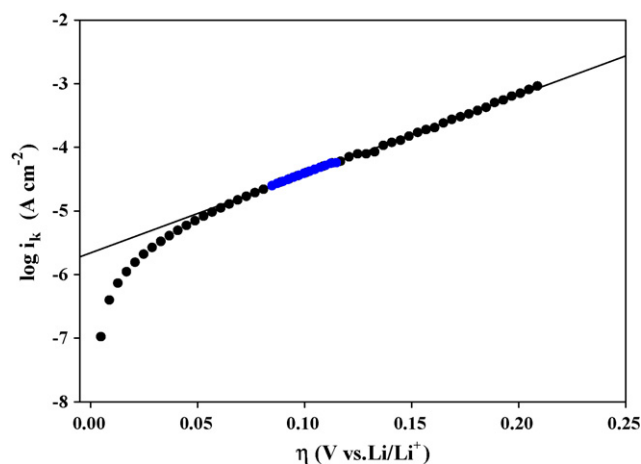


Fig. 4. Tafel plots for ferrocene oxidation at room temperature on a glassy carbon electrode at 2500 rpm for anodic sweep from 3.145 V to 3.35 V at 10 mV s⁻¹ (OCV 3.145 V vs. Li/Li⁺).

for diffusion. In order to correct the measured currents for diffusion, the kinetic current in the mixed activation-diffusion region is calculated from Eq. (6) [24].

$$i_k = \frac{i_{\text{lim}} \cdot i}{i_{\text{lim}} - i} \quad (6)$$

A plot of $\log i_k$ against overpotential, η , should be linear, leading to the Tafel slope b , from which the transfer coefficient, α can be determined [25]. As already stated (Fig. 3) the RDE experiments related exclusively to the oxidation of ferrocene. Fig. 4 shows the Tafel plot from the anodic region of the voltammogram beginning with the open circuit potential (OCV) of 3.145. In this plot, the Tafel region starting at about 60 mV positive of the OCP is clearly delineated from the Butler Volmer region below that. A single Tafel slope of c.a. 79 mV/decade was obtained in the entire potential range for all rotation rates. This slope is analogous that obtained by Petrocelli and Paolucci [26] for the oxidation of potassium ferricyanide in NaOH on platinum. This implies that the initial electron transfer is the rate-limiting step of this reaction. The heterogeneous kinetics of this reaction is so rapid that over a wide range of sweep rates, the reaction is reversible. From this data we calculated the transfer coefficient $\alpha=0.3$, which is comparable to previous ferrocene experiments in aprotic solvents [27,28]. The observed values of Tafel slope and α are indicative of strong interactions between the ferrocenium ions and PF₆⁻ as well as the solvents. The low α also suggests that the structure of the activated complex for the oxidation reaction is closer to that of the oxidized specie. As we noted earlier about 8% of ferrocenium ions are not available for reduction back to ferrocene. This together with the kinetic information suggest a chemical step, following the one-electron rate determining oxidation reaction, in which the ferrocenium ion formed is stabilized by the solvent as well as some of it being transformed into products. This is not unreasonable considering the dipolar nature of the organic carbonate solvents. Extrapolating the Tafel line to equilibrium potential provides the exchange current density (I_0) of $2.0 \times 10^{-6} \text{ A cm}^{-2}$. The rate constant of the electron transfer (anodic oxidation in this case), k^0 , is proportional to I_0 according to

$$I_0 = nFAk^0C \quad (8)$$

We obtained a rate constant of $k^0 = 1.4 \times 10^{-3} \text{ cm s}^{-1}$ from the exchange current density using Eq. (8). Our results show that RDE technique can be successfully applied to highly concentrated electrolyte solutions. The data revealed defined limiting currents from which the kinetics of the system can be deciphered.

4. Conclusions

A detailed study of the kinetics of the oxidation of ferrocene in a concentrated lithium ion conducting electrolyte was carried out using cyclic and rotating disk electrode voltammetry. The results obtained show that the ferrocene–ferrocenium redox couple is reversible in this medium. The values for ferrocene and ferrocenium ion diffusion coefficients were determined from these data. In addition, the electron transfer rate constant (k^0) and the exchange current density (I_0) for the oxidation of ferrocene were calculated. A comparison of the kinetic data obtained from the two electrochemical techniques appears to show that the data from the RDE experiments are perhaps more reliable, because they are collected under strict mass transport control. A Tafel slope of c.a. 79 mV/decade and a transfer coefficient α of 0.3 obtained from analysis of the RDE data suggest that the structure of activated complex in the oxidation reaction of ferrocene is closer to that of the oxidized specie, probably due to strong interactions with PF_6^- and carbonate solvents. Strong interactions between the ferrocenium ion and the carbonate solvent is consistent with the highly dipolar nature of the organic carbonates.

Our results indicate that useful electrochemical kinetic data for soluble redox species in highly concentrated electrolyte solutions relevant to Li-ion batteries can be obtained using the complementary CV and RDE techniques. Such kinetic data are relevant to the studies of redox reagents for overcharge protection of Li-ion batteries, particularly in simulation studies aimed at understanding their performance in practical batteries, and in the development of improved materials.

Acknowledgement

Financial support was provided by the US Army CERDEC through Subcontract No. GTS-S-6-1-437.

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