JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) 298–302

A polyacrylonitrile-based gelled electrolyte: electrochemical kinetic studies

G. NAGASUBRAMANIAN, A. I. ATTIA, G. HALPERT

Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA

(Received 2 September 1992; revised 27 April 1993)

The bulk and interfacial properties of thin films of a polyacrylonitrile-based (PAN-based) gelled electrolyte, which was tested in conjunction with lithium electrodes, were evaluated at room temperature. The typical composition of the gelled electrolyte (GE) studied was PAN (9.13 wt %); propylene carbonate, or PC (84.87 wt %); and $LiBF_4$ (6 wt %). A.c. and d.c. measurements were used to determine the bulk conductivity and the interfacial apparent charge-transfer resistance (R_{act}) of the GE. While the bulk conductivity remains stable at around 10^{-3} S cm^{-1}, the R_{act} varies initially before reaching a steady value. The steady R_{act} value obtained from the electrochemical measurements is near 1000 Ω cm^2. The plating/stripping efficiency of lithium, from potentiostatic and galvanostatic measurements, is 70 to 80%.

1. Introduction

Solid electrolytes that exhibit high ionic conductivity have generated, in recent years, widespread interest as potential candidate materials for a variety of applications, including solid-state batteries, chemical sensors, and fuel cells [1]. The pioneering work of Armand *et al.* [2] and others [3, 4] led to the development of polymer-based electrolytes for battery applications. Although these studies, especially the one on polyethylene oxide, caused an explosion of research on high-ionic-conductivity polymer materials, fundamental problems prohibit these materials from being used as electrolytes in batteries. Specifically, the lack of a solid electrolyte with reasonable room-temperature ionic conductivity is a major drawback. However, more than 16 years ago, Feuillad and Perche [5] reported the use of polyvinylacetal-based and polyacrylonitrile-based (PAN-based) ion-conductive membrane gels as separators in Li–CuS batteries. More recently, Watanabe *et al.* [6] reported a novel idea to improve the ionic conductivity: trapping an organic liquid in a polymer matrix. The so-called gelled electrolyte (GE) combining either polyvinylidene fluoride or PAN with $LiClO_4$ and ethylene carbonate exhibits room-temperature conductivity ranging from 10^{-4} to 10^{-8} S cm^{-1}, depending on the composition. The clue that the ionic conductivity of the gelled electrolytes could be varied by a judicious combination of the structure and composition has been exploited lately by different schools [7, 8], with encouraging results. However, no fundamental electrochemical data on factors that control and govern the performance of the GEs are available. Our present study aims at evaluating the basic electrochemical parameters of the GE comprising PAN, $LiBF_4$, and propylene carbonate (PC), and the results of our study are described below.

2. Experimental details

All the chemicals used in this study were purchased from Aldrich Chemical Company. Thin films of GE comprising PAN, $LiBF_4$, and PC were prepared as follows. Appropriate amounts of PAN (2.9 g), $LiBF_4$ (1.87 g), and PC (12.66 cm^3, or 15.06 g) were weighed into a glass beaker and mixed for 10 to 15 min inside an argon-filled glove box. (To ensure complete dissolution and to compensate for the losses, a small quantity of excess PC, included in these numbers, was added.) The temperature of the mixture was slowly raised to 120° C, with constant stirring. The clear, pale-yellow solution was transferred quickly to Teflon moulds (which were weighed beforehand when empty). The fluid solidified quickly, and the Teflon moulds, with the solid fluid, were weighed again before being transferred to a vacuum oven. They were pumped for 24 h, and then the Teflon moulds were weighed again. The final composition of the GE, as computed from the three weights, was PAN, 9.13 wt %; $LiBF_4$, 6 wt %; and PC, 84.87 wt %.

The equipment used for the electrochemical measurements and the cell fixtures is described elsewhere [9]. The electrochemical cells were assembled either in an argon-filled glove box or in a dry room. The electrolyte area is about 0.8 cm^2, and the electrolyte thickness is around 100 μm.

3. Results and discussion

The bulk and interfacial properties of the electrolyte govern, respectively, the charge/discharge rates and

0021-891X 1994 Chapman & Hall

the cycle life of the cell. In this study, the bulk and interfacial properties of the GE films were characterized by the use of several electrochemical techniques. These include (i) a.c. impedance, (ii) d.c. measurements (linear polarization, Tafel plots, and galvanostatic measurements at short times). In addition, the plating/stripping efficiency of lithium was determined from both potentiostatic and galvanostatic measurements.

3.1. *A.c. measurement*

Small-amplitude (small enough not to induce nonlinear response) a.c. measurements as a function of frequency can reveal different processes occurring at different time domains [10]. The bulk and charge-transfer (with a finite charge-transfer resistance) processes occur, respectively, at the high and low ends of the frequency spectrum [11]. The a.c. measurements of ideal cells of symmetrical structure (cells comprising an ionically conducting electrolyte sandwiched between nonblocking electrodes) will yield the bulk resistance (R_b) of the electrolyte and other ohmic components, as well as the interfacial apparent-charge-transfer resistance (R_{act}) of the ion of the nonblocking electrode (Fig. 1(a)). ($R_{act} = (R_i + R_{ct})$ is one-half of the diameter of the semicircle in a Nyquist plot for a symmetrical cell). In the plot, the semicircle, at high frequencies, belongs to the kinetic-control regime, and the straight line, which has a frequency-independent phase angle of $\pi/4$, belongs to the diffusional-control regime. A typical Nyquist plot in the frequency regime of 100 kHz to 0.01 Hz at open-circuit voltage (o.c.v.) is given in Fig. 1(b) for the cell Li/GE/Li (o.c.v. is 0.0 V in this case). The high-frequency intercept in Fig. 1(b) is the bulk resistance of the gelled electrolyte and other ohmic components. The low-frequency intercept varies with time before reaching a steady value. The resistance associated with the diameter of the semicircle shown in Fig. 1(a) has unequivocally been shown to be the resistance of the interphase (interfacial layer arising from the reaction of lithium with the electrolyte and/or salt) [12]. Note in Fig. 1(b) the absence of Warburg (diffusional) impedance at very low frequencies (< 100 mHz). The frequency range of the diffusion behaviour is controlled by the diffusion coefficient of the mobile ion, in this case Li^+, and the thickness of the film through which Li^+ is diffusing. In an ideal case, the impedance phase angle in the diffusion regime is $\pi/4$ and is independent of frequency. The absence of Warburg impedance was earlier reported by others for polyethylene oxide electrolytes [13] and was attributed to the interphase omnipresent at the lithium/electrolyte interface. To gain further insight into the formation and dissolution of the interphase, we did galvanostatic measurements followed by a.c. measurements. Galvanostatically, at 0.1 mA rate, we stripped lithium from a symmetrical cell and plated it on again. Nearly one-fourth of the capacity of lithium was stripped and replated. The measurement was repeated several times on both the electrodes, to establish that the lithium interfaces on both sides of the electrolyte were identical, before a.c. measurements were performed. The result of the a.c. measurement, performed immediately after the lithium plating/stripping measurement, is given in the form of a Nyquist plot in Fig. 2. The plot shows the low-frequency intercept (the diameter of the semicircle)

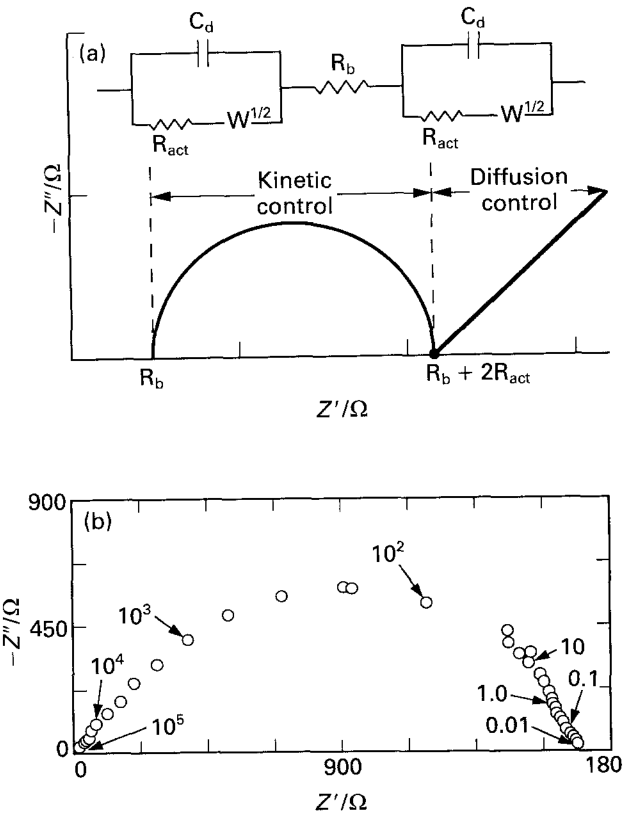

Fig. 1. (a) Ideal complex impedance behaviour expected of the equivalent circuit shown at the top. (b) Nyquist plot of the Li/GE/Li cell in the frequency regime 100 kHz to 10 mHz. R_b represents the bulk resistance of the GE; R_{act} is the interfacial apparent charge-transfer resistance. Measurements were taken at 25° C.

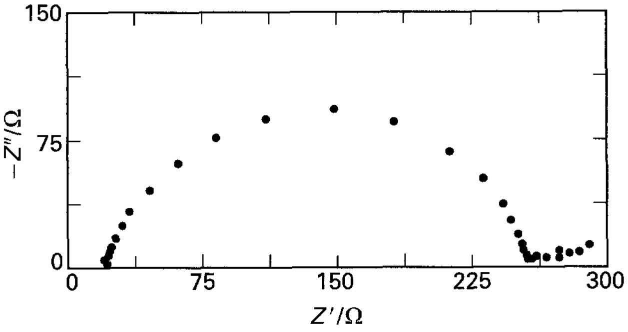

Fig. 2. Nyquist plot of the cell in Fig. 1(b) after galvanostatically cleaning the Li/GE interface (see text). The frequency regime and temperature employed were the same as those used for Fig. 1(b).

is smaller than in Fig. 1(b), and, more importantly, there is a diffusional line in the frequency regime 100 to 1 mHz. Also note that the phase angle is not $\pi/4$, the value for an ideal case. Two tentative, separate conclusions that one could draw from this observation are (i) the interphase is not dissolved completely or (ii) the fresh lithium exposed to the electrolyte because of the dissolution of the interphase reacts instantaneously with the electrolyte, forming an interfacial layer. The second speculation seems more plausible, in the present work, since the large amount of charge passed in the galvanostatic measurements would certainly have dissolved the interphase. Subsequent a.c. measurements as a function of time show the progressive growth of the semicircle and the disappearance of the Warburg impedance. These results suggest that an interfacial layer between lithium and electrolyte continues to form and that it may be impossible to achieve an interphase-free lithium electrolyte interface. Also, our a.c. data seem to support the idea that the interphase does not grow continuously, but stops growing after reaching a certain thickness, as shown by a near-constant low-frequency intercept value as a function of time. Further, our observations seem to suggest that it may never be possible to separate the interphase resistance (R_i) and the charge-transfer resistance (R_{ct}) in the lithium gelled electrolyte systems. In a practical cell, since the Li^+ sees only the total resistance ($R_i + R_{ct}$), we define the total resistance as apparent charge-transfer resistance (R_{act}).

The average electrolyte bulk resistivity computed from such plots is 1000 to 1200 Ω cm^2, which is comparable to that of liquid electrolytes. The R_{act} varies initially and reaches a stable value of 1000 Ω cm^2. The double-layer capacitance (C_{dl}) consisting of electrolyte/interphase and lithium/interphase capacitances is around 3 μF. A.c. measurements were also carried out on GE thin films sandwiched between two well-polished, flat, stainless steel (SS) electrodes. In Fig. 3, the Nyquist plot of one such measurement is shown. The plot exhibits a typical capacitive behaviour, and the real-axis intercept gives the resistance of the electrolyte. The resistivity computed from the plot is comparable to that obtained from Fig. 1(b).

3.2. *D.c. measurements*

The open-circuit voltage immediately after assembly of an Li/GE/SS cell is about 3 V, which is almost the potential of lithium against SS. This observation suggests that the lithium is in ionic contact with the SS electrode. The importance of this observation is that the interphase between lithium and GE is also a lithium ion conductor [12].

3.2.1. Linear polarization plots and Tafel plots. Typical linear-polarization plots and Tafel plots for a symmetrical cell are given, respectively, in Figs 4 and 5 (the cell is Li/GE/Li, which is the same one represented in Fig. 1(b)). The R_{act} and transfer-coefficient (α), which is obtained from an equation, Tafel slope $= RT/2.303\alpha$, are given for different techniques in Table 1. While the R_{act} is comparable to that from the a.c. measurement, the near-identical values of the Tafel slopes in both directions suggest a facile, reversible Li^+ transfer at the interface. The apparent exchange current density (I_0) for lithium determined by use of the formula $I_0 = (RT/nF)/R_{act}$, is 0.05 mA cm^{-2}.

3.2.2. Galvanostatic measurements at short times. Galvanostatic measurements at different current

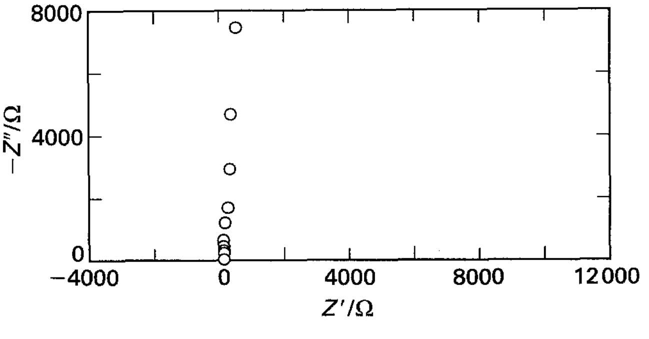

Fig. 3. Nyquist plot of SS/GE/SS cell in the frequency regime 100 kHz to 10 mHz at 25° C. 'SS' represents 'stainless steel electrode'.

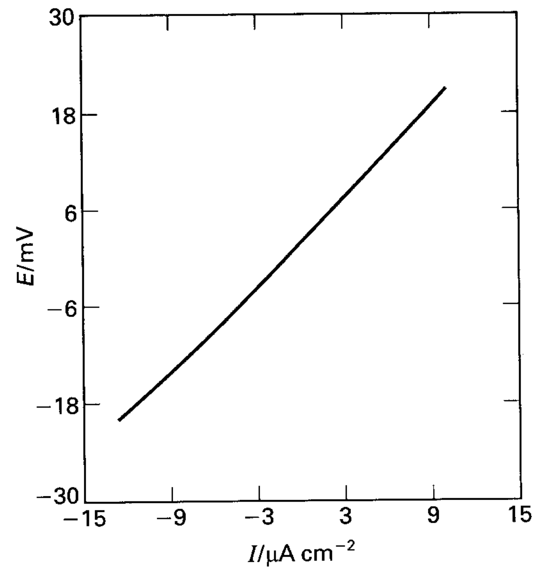

Fig. 4. Linear polarization of the cell Li/GE/Li. The scan rate is 0.1 mV s^{-1}.

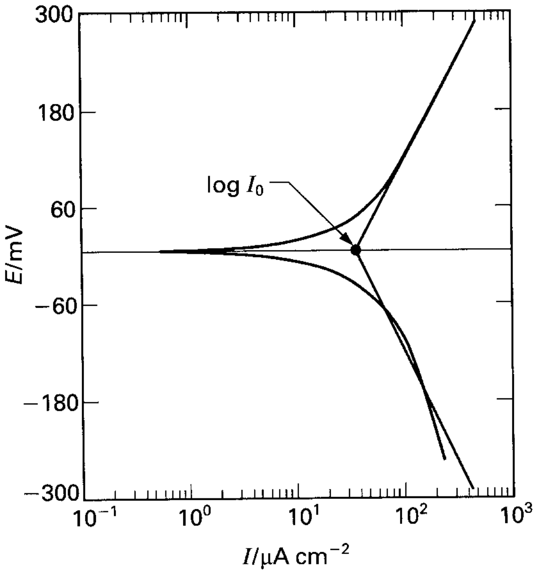

Fig. 5. Tafel plot of the cell Li/GE/Li. The scan rate is 0.1 mV s^{-1}.

amplitudes, in the range 25 to 500 μA, were made of symmetrical cells (Li/GE/Li cells, the same as those discussed in Fig. 1(b)) to compute the total resistance of the cell. The voltage jump is proportional to the d.c. current, indicating the absence of any nonlinear process in the cell, which in turn supports the simple equivalent circuit proposed in Fig. 1(a). This method yielded similar R_{act}, as shown in Table 1.

3.2.3. Plating/stripping efficiency of lithium: potentiostatic method. The cell used for this study is an unsymmetrical cell of type SS/GE/Li, where 'SS' denotes stainless steel. The potential was scanned at 0.1 mV s^{-1} between −0.1 and 0.25 V. The voltammogram (not shown here) shows a good reversibility with coulombic efficiency in the range of 80%. The coulombic efficiency is rather low and is mainly attributed to the reactivity of the cyano group in the polyacrylonitrile toward lithium.

3.2.4. Plating/stripping efficiency of lithium: galvanostatic method. The average lithium cycling efficiency was computed (for the cell used in the potentiostatic method) by using the following equation [14, 15]

$$X = \{q_c - [Xq_i - q_f]/n\}/q_c$$

where X is the average cycling efficiency per cycle, q_c is the charge plated or dissolved per cycle, q_i is the charge involved in the initial deposition, q_f is the charge involved in the final dissolution of lithium, and n the total number of cycles.

The capacity of the lithium electrode was around 90 C (25 mAh). In the first cycle, 9.9 C (q_i) were plated, and in the next cycle, 3.3 C (q_c) were either dissolved or plated. In each of the subsequent cycles, the same amount of charge was either dissolved or plated. Finally, the total coulombs (q_f) of lithium stripped from the SS electrode was 8 C. The value of X is greater than 80%. Both the potentiostatic and galvanostatic methods gave similar plating/stripping lithium efficiency.

Table 1. Fundamental electrochemical parameters of the GE

Techniques	$R_{act}/\Omega\,cm^2$	α_{anodic}	$\alpha_{cathodic}$
Linear polarization	980	–	–
Tafel	980	0.49	0.51
Galvanostatic	980	–	–

4. Conclusions

The R_{act} obtained from the a.c. measurements and the d.c. measurements are comparable. The electrolyte bulk conductivity is of the order of 10^{-3} S cm^{-1}, which is comparable to that of liquid electrolytes. Not only do the similar transfer-coefficient values from both the anodic and cathodic branches in the Tafel plot indicate a reversible Li$^+$ transfer at the interface; also, the apparent exchange current density, which indicates the rapidity of a chemical reaction, is high and may allow and sustain a fast rate. The lithium plating/stripping efficiency is around 80%, which is low and suggests the reactivity of the Li/GE interface.

Acknowledgement

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

References

[1] G. C. Farrington and J. L. Briant, *Science* 4 (1979) 1371; 'Solid Electrolytes and Their Applications', (edited by E. C. Subbaro), Plenum Press, NY (1980).

[2] M. B. Armand, J. M. Chabagno and M. J. Duclot, 'Fast Ion Transport in Solids', (edited by P. Vashishta, J. N. Mundy and G. K. Shenoy), Elsevier, North Holland, NY (1979) p. 131.

[3] D. E. Fenton, J. M. Parker and P. V. Wright, *Polymer* **14** (1973) 589.

[4] W. I. Archer and R. D. Armstrong, *Electrochim. Acta.* **25** (1980) 1689; *ibid.* **26** (1981) 167.

[5] G. Feuillade and Ph. Perche, *J. Appl. Electrochem.* **5** (1975) 63.

[6] M. Watanabe, M. Kanba, K. Nagaoka and I. Shinotvara, *J. Polym. Sci. Polym. Physics* **21** (1983) 939.

[7] D. G. Fauteux, M. J. Moore and P. M. Blonsky, *US Patent 4 925 752* (15 May, 1990).

[8] K. M. Abraham and M. Alamgir, *J. Electrochem. Soc.* **137** (1990) 1657.

[9] G. Nagasubramanian and S. Di Stefano, *ibid.* **137** (1990) 3830.

[10] Y. Uchimoto, Z. Ogumi, Z. Takehara and F. R. Foulkes, *ibid.* **137** (1990) 35.

[11] P. G. Bruce and F. Krok, *Electrochim. Acta* **33** (1988) 1669.

[12] D. Fauteux, *Solid State Ionics* **17** (1985) 133.

[13] B. Scrosati, *J. Electrochem. Soc.* **136** (1989) 2774.

[14] D. Aurbach, O. Youngman, Y. Gofer and A. Metan, Electrochim. Acta **35** (1990) 625.

[15] D. Aurbach, Y. Gofer and J. Langzan, J. Electrochem. Soc. **136** (1989) 3198.