

Electrochemical behaviour of aluminium in non-aqueous electrolytes over a wide potential range

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Abstract

The electrochemical behaviour of aluminium in LiClO₄–propylene carbonate electrolyte is studied by cyclic voltammetry, steady-state polarisation, and ac impedance spectroscopy in the potential range –0.4–4.2 V versus Li/Li⁺. The open-circuit potential of Al is 1.57 V versus Li/Li⁺, which is about 0.2 V above the thermodynamic value of Al due to the presence of a surface passive film. In the positive potential region, Al is fairly stable between 1.57 and 3.5 V versus Li/Li⁺ owing to the presence of the surface film. Nevertheless, the oxidation of Al occurs at potentials >3.5 V versus Li/Li⁺. The ac impedance data are analysed by using a non-linear least-squares fitting procedure, and the surface film resistance is found to be between 498 and 1032 kΩ cm⁻². In the potential range 3.6–4.2 V versus Li/Li⁺, there is a breakdown of the passive film as demonstrated by a decrease in its resistance to 1.2–4.8 kΩ cm⁻². This breakdown accompanies anodic oxidation of Al. Thus, there is a possibility of anodic degradation of the Al substrate that is usually used as the current-collector of positive electrodes of Li-ion batteries, if Al is exposed to the electrolyte. In the negative potential region, the deposition of uniform and non-dendritic Li occurs, which can be anodically stripped in a quasi-reversible process with high coulombic efficiency. Diffusion of Li into Al results in the formation of a surface layer of Li–Al alloy, as suggested by X-ray diffraction patterns. The quasi-reversible cathodic deposition and anodic stripping of Li with an exchange current density of 0.16 mA cm⁻² indicates that Al is useful as a negative electrode in Li-batteries. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Aluminium oxidation; Surface film; Lithium deposition; Cyclic voltammetry; Alternating current (ac) impedance

1. Introduction

Research and development efforts on high-energy batteries have assumed considerable importance in recent years [1]. The lithium-ion battery has emerged as the most promising energy-storage device for a wide range of applications [2,3]. This battery consists of a lithiated transition metal oxide (e.g. LiCoO₂) as the positive electrode active material and carbon (e.g. graphite) as the negative electrode active material. The cell is electrochemically active due to intercalation–de-intercalation of Li⁺ ions at both the electrodes. The potential of the positive electrode is about 4.2 V versus Li/Li⁺ and that of the negative electrode is close to 0 V versus Li/Li⁺.

The current-collectors generally employed for the positive and negative electrodes are Al and Cu, respectively. It is noteworthy that the potential of Al is 1.37 V versus Li/Li⁺, a

value that is extremely negative with respect to the positive electrode. Due to the presence of porous active materials on the surface, the potential of Al wherever it is not covered by the electrode active material shifts to a high positive value. Consequently, it is susceptible to oxidation. Furthermore, if cell reversal, which may happen in the case of a battery due to the mismatch of the capacity of individual cells, occurs, the potential of Al shifts to negative values where the reduction of Li⁺ ions is possible. An evaluation of electrochemical characteristics of Al over a wide potential range in non-aqueous media is therefore important. There are few reports on this topic in the literature [4–6]. For example, a bare Al electrode in a non-aqueous electrolyte has been cycled repeatedly between 3 and 4.2 V versus Li/Li⁺, and the surface morphology examined [4]. Mounds containing Al and Al₂O₃ as well as pits on the surface, have been identified. By measuring the ac impedance response of the electrode, pitting resistance has been shown to increase with the number of electrical cycles. The corrosion behaviour of Al current-collectors in Li/polymer batteries has

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been reported by Chen et al. [5]. In contrast to the studies reported in non-aqueous electrolytes [4], Al has been shown to possess resistance to uniform corrosion in polymer electrolytes during normal battery charging. Large currents of galvanostatic polarisation bring about the breakdown of Al_2O_3 films, however, and pitting corrosion occurs. In a study of the anodic oxidation of Al in propylene carbonate by means of electrochemical measurements, microscopic observations, elemental and gravimetric analyses, it has been found that the formation and growth of the oxide on Al occurs in the early stages of anodization [6]. Further anodic oxidation leads to the breakdown of part of the oxide film, which results in pitting corrosion. In all these studies, the behaviour of Al in only the positive potential range has been studied. There are no reports of studies over a wide potential range encompassing both the anodic and cathodic regions in non-aqueous lithium battery electrolytes.

In the present study, the electrochemical behaviour of Al is investigated in LiClO_4 -propylene carbonate electrolyte over the potential range -0.4 – 4.2 V versus Li/Li^+ . The results suggest that, in the positive potential range, Al can undergo oxidation at potential values >3.6 V, accompanied by breakdown of surface film. In the negative potential range on the other hand, deposition of Li occurs on Al at close to 0 V versus Li/Li^+ . The deposition of Li is uniform without the formation of dendrites, and deposition-stripping cycles occur with good coulombic efficiency. The results suggest that Al is a promising substrate material for Li electrodes.

2. Experimental

Propylene carbonate, LiClO_4 and Li metal were purchased from Aldrich. Propylene carbonate was vacuum distilled at about 120°C and treated with molecular sieves of porosity 4 \AA before making solutions. LiClO_4 was dried at 100°C . Lithium electrodes were sectioned out of a ribbon of 0.75 mm thickness and the surface was abraded before cell assembly. Aluminium electrodes were cut from a high purity Al sheet of 0.5 mm thickness polished to a smooth finish, washed copiously with distilled water rinsed with acetone, dried in a vacuum desiccator, and transferred into a dry box.

Preparation of electrolytes and the assembly of cells were performed in an argon atmosphere in a dry box (MBraun model Unilab) with impurities of moisture and oxygen <10 ppm each. The electrochemical cells were assembled in glass containers with airtight stoppers made of PTFE and provided with electrical leads. The aluminium foil working electrode had an area of 1.2 cm^2 exposed to the electrolyte. Lithium foil was used for the auxiliary and reference electrodes. All potential values are reported with respect to the Li/Li^+ reference electrode.

Cyclic voltammetry and electrochemical impedance measurements of the cells in three-electrode configuration were performed using an EG&G PARC potentiostat-galvanostat (model Versastat) and an electrochemical impedance ana-

lyser (model 6310), respectively. For galvanostatic deposition and anodic stripping of Li, an electrical circuit that consisted of a regulated dc power source, a high resistance, and an ammetre in series with the electrochemical cell was employed. A high input impedance digital multimeter was used for measuring electrode potentials. X-ray diffraction patterns of the Al foils were recorded using a Scintag powder X-ray diffractometer (model XDS 2000) with a copper source. Surface morphology was examined with a JEOL scanning electron microscope (model JSM 5600LV). Electrochemical experiments were performed in an air-conditioned room maintained at $20 \pm 1^\circ\text{C}$.

3. Results and discussion

3.1. Positive potential range

The open-circuit potential of Al is about 1.57 V versus Li/Li^+ , independent of the concentration of LiClO_4 in propylene carbonate electrolyte. The cyclic voltammogram of Al recorded at a scan rate of 0.05 V s^{-1} in the potential range 1.57 – 4.2 V in 1 M LiClO_4 electrolyte is shown in Fig. 1. During the forward sweep, there is an initial increase in current until the potential reaches about 2.5 V. Following this, the current is nearly invariant between 2.5 and 3.5 V, but starts to increase at about 3.5 V, and reaches a value of about $80 \mu\text{A cm}^{-2}$ at 4.2 V. This suggests that Al is anodically stable due to the presence of a surface film at potentials

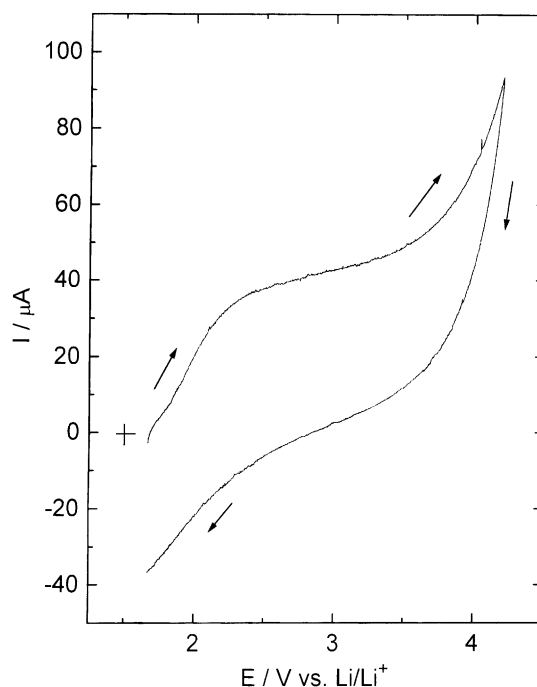


Fig. 1. Cyclic voltammogram at 0.05 V s^{-1} showing anodic behaviour of Al electrode (area = 1.2 cm^2) in 1 M LiClO_4 -propylene carbonate electrolyte.

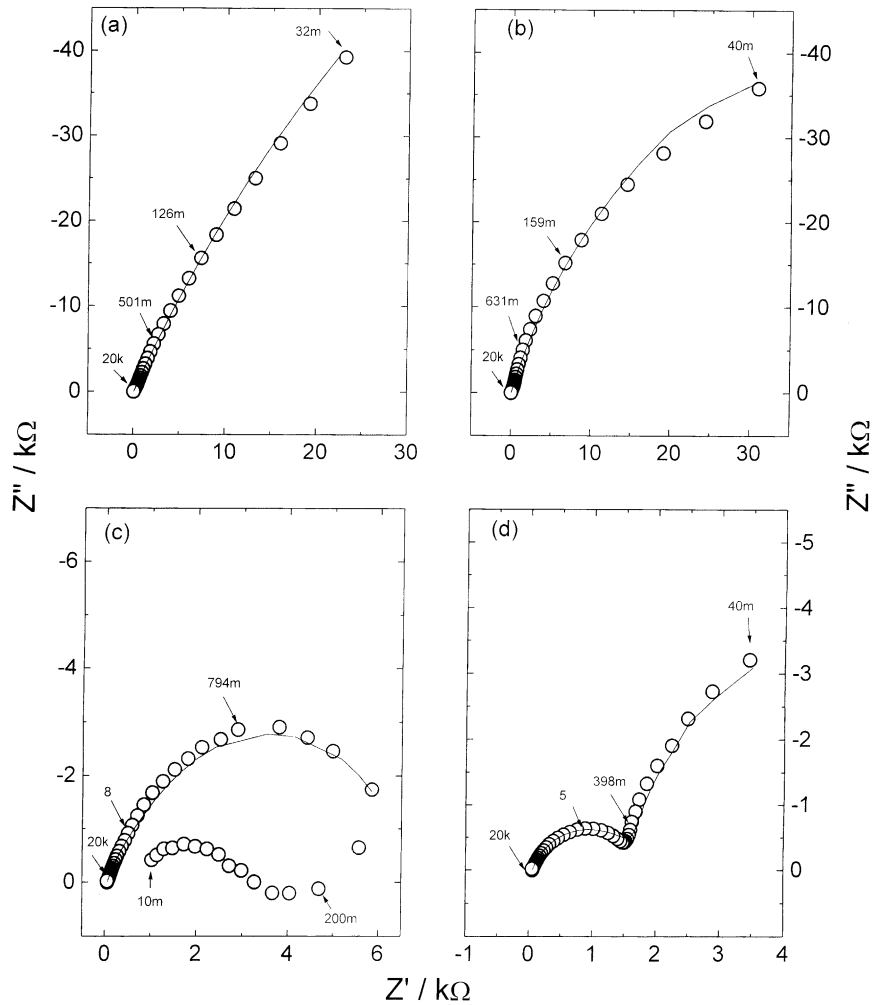


Fig. 2. Nyquist impedance spectra of Al electrode (area = 1.2 cm²) at different potentials: (a) 1.57, (b) 3.44, (c) 3.66, (d) 4.22, V versus Li/Li⁺. Experimental data are shown as symbols and simulated spectra from NLLS fit results as curves. Frequency values (Hz) of some data points are shown.

<3.5 V and that it undergoes oxidation above this potential, i.e.,



There are two possibilities for the presence of a surface film on Al. First, there can be a native oxide film prior to cell assembly in the non-aqueous electrolyte. Second, the oxidation current between 1.57 and 2.5 V (Fig. 1) is possibly due to oxidation of Al to Al³⁺ producing Al₂O₃ or Al₂(CO₃)₃ on the surface akin to the mechanism of formation of surface films on Li [2]. The formation of Al₂O₃ films on Al in non-aqueous electrolytes has been reported [4,7]. As a result, the Al electrode acquires surface passivity towards anodic oxidation up to about 3.5 V. At potentials >3.5 V, reaction 1 occurs via the breakdown of the surface oxide film. This is reflected by a decrease in the resistance of the Al electrodes, as discussed below.

Electrochemical impedance spectra of Al measured at different potential values between 1.5 and 4.2 V (Fig. 2) corroborate the cyclic voltammetric data. Nyquist plots (Fig. 2) of the impedance spectra between 1.5 and 3.5 V

do not take the shape of semicircles. These data may be explained with the help of equivalent circuit shown in Fig. 3(a), where the resistance (R₁) and capacitance (C₁) of the surface layer are considered to exist in parallel combination and the solution resistance (R₀) is in series.

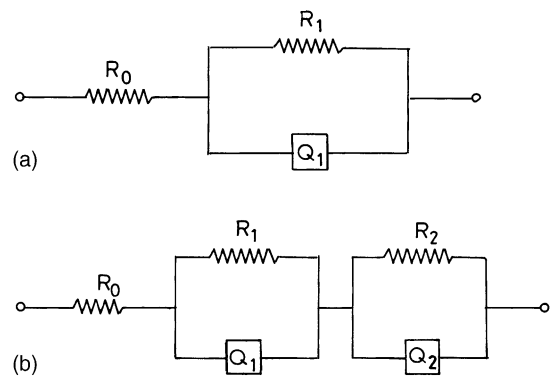


Fig. 3. Equivalent circuits used for NLLS fitting of experimental data (see text for symbols) of Al electrode.

Table 1
Impedance parameter obtained by NLLS fit at different potentials

Potential (V)	Equivalent circuit	Parameters						
		R_0 (Ω)	R_1 (Ω)	Q_1	n_1	R_2 (Ω)	Q_2	n_2
1.57	R (RQ)	55.7	4.15×10^5	7.04×10^{-5}	0.75			
1.85	R (RQ)	57.0	4.84×10^5	6.43×10^{-5}	0.76			
2.33	R (RQ)	57.9	5.39×10^5	6.09×10^{-5}	0.78			
2.80	R (RQ)	57.9	7.98×10^5	4.37×10^{-5}	0.81			
3.05	R (RQ)	62.5	8.58×10^5	4.99×10^{-5}	0.82			
3.44	R (RQ)	58.3	1.34×10^5	5.10×10^{-5}	0.80			
3.66	R (RQ) (RQ)	57.5	4.84×10^3	4.55×10^{-5}	1	1.59×10^3	7.04×10^3	0.73
3.85	R (RQ) (RQ)	59.0	1.02×10^3	2.89×10^{-5}	0.83	8.28×10^3	1.59×10^3	1.00
4.12	R (RQ) (RQ)	57.8	1.58×10^3	3.62×10^{-5}	0.80	2.81×10^3	1.81×10^3	1.00
4.22	R (RQ) (RQ)	56.8	1.65×10^3	3.96×10^{-5}	0.79	5.95×10^3	1.04×10^3	1.00

Since impedance parameters such as the capacitance are usually distributed and their values vary over the electrode surface, a constant phase element (CPE) Q_1 is considered in place of C_1 [8]. The impedance spectra in the potential region between 1.57 and 3.5 V have been analysed by means of a non-linear least-squares (NLLS) fitting program due to Boukamp [9]. Values of the parameters obtained at several potentials are given in Table 1. The solution resistance (R_0) is nearly invariant at all potentials, whereas the surface film resistance (R_1) increases from $498 \text{ k}\Omega \text{ cm}^{-2}$ at 1.57 V to $1032 \text{ k}\Omega \text{ cm}^{-2}$ at 3.05 V. As the value of R_1 is high the impedance data are nearly parallel to the imaginary axis (Fig. 2(a) and (b)) and suggest a capacitive behaviour. This is clearly reflected in the Bode form of the impedance data (not shown) where $\log(\text{impedance}, |Z|)$ in the frequency region from 100 kHz to 100 Hz decreases linearly with $\log(\text{frequency})$ with a slope of about 0.9 which is close to the value of unity for a pure capacitor.

At about 3.6 V, the impedance Nyquist spectrum has the shape of a semicircle with a positive loop in the low-frequency region Fig. 2(c) As observed with cyclic voltammetry, oxidation of Al starts around this potential (Fig. 1). As a low-frequency positive loop in an electrochemical process is reported to be due to adsorbed species [10,11] such a loop may be attributed in the case of Al to the adsorption of Al species. Thus, the distorted capacitive semicircle in Fig. 2(c) is due to an overlap of the impedance of the anodic oxidation of Al and the impedance of the surface film. The spectrum (Fig. 2(c)) omitting the low-frequency loop is represented by the equivalent circuit shown in Fig. 3(b), where the charge-transfer resistance (R_2) of reaction (1) and a CPE (Q_2) corresponding to the double-layer capacitance (C_2) are considered to exist in parallel which, in turn, is in series with the rest of the sub-circuit. The semicircle is distorted due to overlap of the R_1C_1 and R_2C_2 time constants. At potentials >3.6 V the data resolve into a pair of semicircles (Fig. 2(d)) due to decrease in the R_2C_2 time constant as a result of an increased rate of reaction (1). The impedance parameters obtained by fitting the data in the potential range 3.5–4.2 V are included in Table 1. It is found that the ohmic resistance

(R_0) is nearly constant throughout the positive potential range. The resistance (R_1) of the surface film on Al is between 498 and $960 \text{ k}\Omega \text{ cm}^{-2}$ in the potential range up to 3 V, but decreases to $1.2\text{--}4.8 \text{ k}\Omega \text{ cm}^{-2}$ in range 3.6–4.2 V. This decrease is attributed to breakdown of the surface film on Al which allows the oxidation of Al (reaction 1) to take place. The decreases in resistance also supports the cyclic voltammetric results, which have indicated an increase in current due to reaction (1) at about 3.5 V. The charge-transfer resistance (R_2) of reaction (1) decreases with increase in potential (Table 1) which suggests an increase in the reaction rate.

3.2. Negative potential range

Electrochemical impedance spectra of Al were recorded at several potentials between the open-circuit potential 1.57 and -0.4 V. The impedance behaviour of Al is capacitive, similar to the data of Fig. 2(a) and (b) down to about 0 V and satisfies the equivalent circuit shown in Fig. 3(a). The data at 0 V and more negative potentials, however, take the shape of semicircles due to deposition of Li according to:



The impedance of Al at 0 V is shown in Fig. 4 as a Nyquist plot. A comparison of Figs. 2 and 4 suggests that the impedance in the latter is lower than that in the former by several orders of magnitude. Under the conditions of deposition of Li on Al, the impedance spectrum corresponds to an equivalent circuit similar to that shown in Fig. 3(a) with R_3 and Q_3 in place of R_1 and Q_1 where the charge-transfer resistance (R_3) of reaction (2) is considered in parallel with Q_3 . The CPE Q_3 is used in place of the double-layer capacitance (C_3) of the Li(on Al)/electrolyte interface. The impedance spectrum (Fig. 4) has been analysed by the NLLS fitting procedure and the values of the parameters are included in the caption of Fig. 4. The values of the charge-transfer resistance (R_3) obtained is $47.4 \text{ }\Omega \text{ cm}^{-2}$ which is a value similar to that obtained from dc polarisation data and the exchange current density of reaction (2), as calculated in the manner described below.

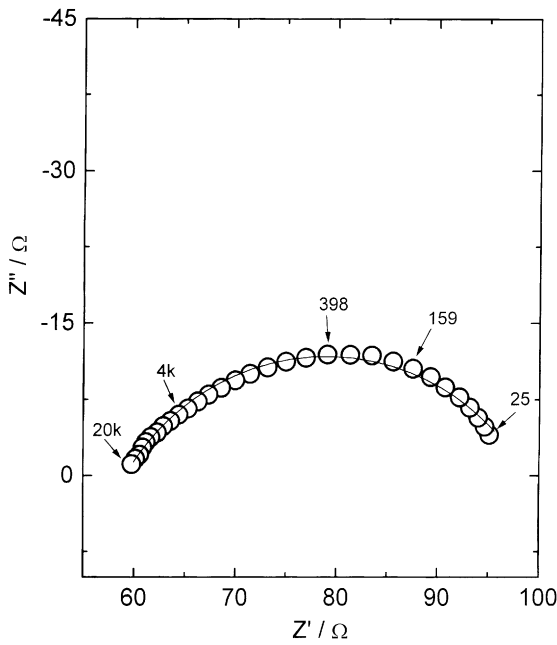


Fig. 4. Nyquist impedance spectrum of Al electrode (area = 1.2 cm²) at 0 V in 1 M LiClO₄-propylene carbonate electrolyte. Experimental data are shown as symbols and simulated spectrum from NLLS fit results as a curve. Values of fit parameters are: $R_0 = 59.2 \Omega$, $R_3 = 39.5 \Omega$, $Q_3 = 1.17 \times 10^{-4}$, and $n_3 = 0.681$. Frequency values (Hz) of some data points are shown.

The cathodic deposition of Li on Al surface was further studied by cyclic voltammetry. The cyclic voltammograms recorded between 2.5 and -0.6 V are presented in Fig. 5. During the forward sweep, current starts increasing at about

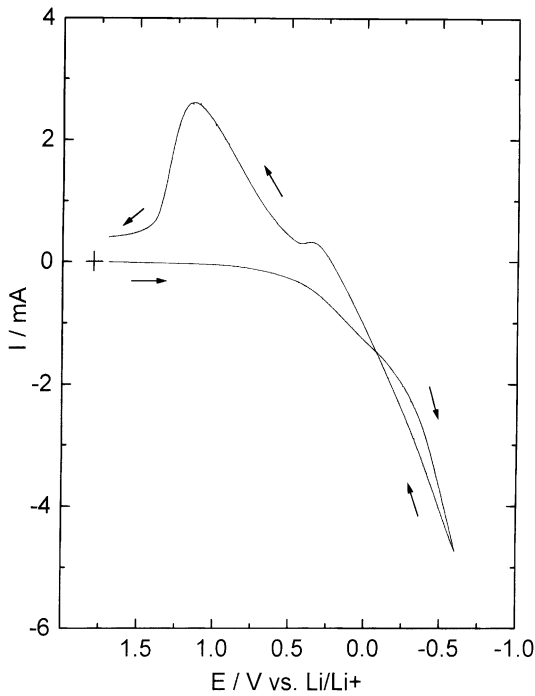


Fig. 5. Cyclic voltammogram at 0.05 V s⁻¹ showing cathodic behaviour of Al electrode (area = 1.2 cm²) in 1 M LiClO₄-propylene carbonate electrolyte.

0 V and continues without reaching any peak. The large magnitude of the cathodic current is due to reduction of Li⁺ (reaction 2) and results in the deposition of Li on the surface. The absence of a current peak in the cathodic direction suggests that the deposition of Li is under charge-transfer control. The surface of Al turns grey in this region. During the reverse sweep, the current peaks at about 0.8 V, which is attributed to diffusion-limited anodic oxidation of Li on the Al surface (reverse of reaction 2). Thus, the deposition of Li on Al occurs as a charge-transfer-controlled process whereas the reverse reaction occurs as a diffusion-limited process. It is interesting to note that, upon completion of the potential cycle, the surface of the Al remains grey, which indicates the presence of Li on Al. This suggests that the amount of Li deposited in the forward sweep is not completely oxidised back into the electrolyte. This conclusion is supported by the fact that the charge associated with the anodic current is less than the cathodic charge of Li deposition.

The cathodic deposition of Li on Al was carried out galvanostatically at a current of 0.83 mA cm⁻² for several hours. It was found that the deposition was smooth and uniform, without any dendrites. Under similar experimental conditions with Li instead of Al, the Li deposited was spongy and dendritic. Subsequently, Li on Al electrode was stripped by anodic discharge. and then the galvanostatic charge-discharge cycling continued. The variation of electrode

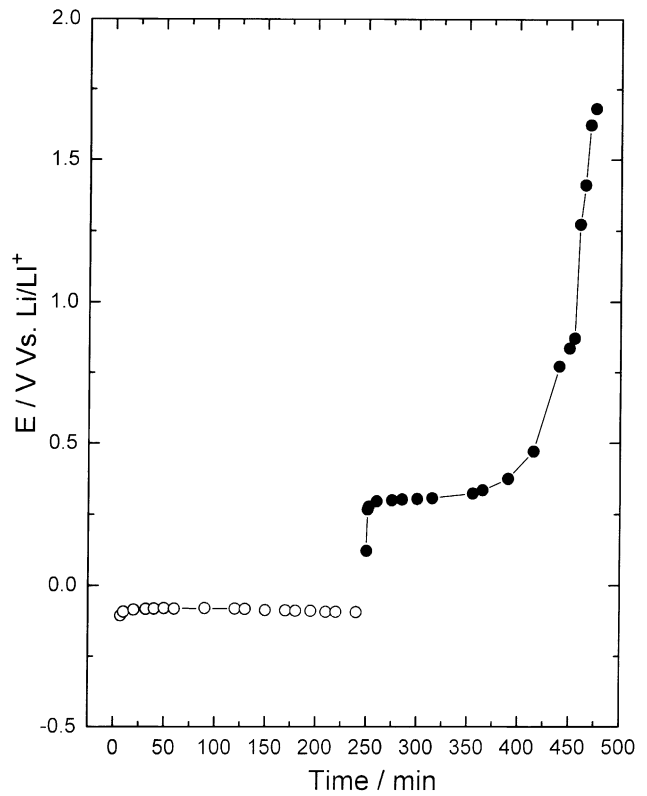


Fig. 6. Variation of Al electrode potential during deposition (○) and stripping (●) of Li at current density of 0.83 mA cm⁻² in 1 M LiClO₄ in propylene carbonate electrolyte.

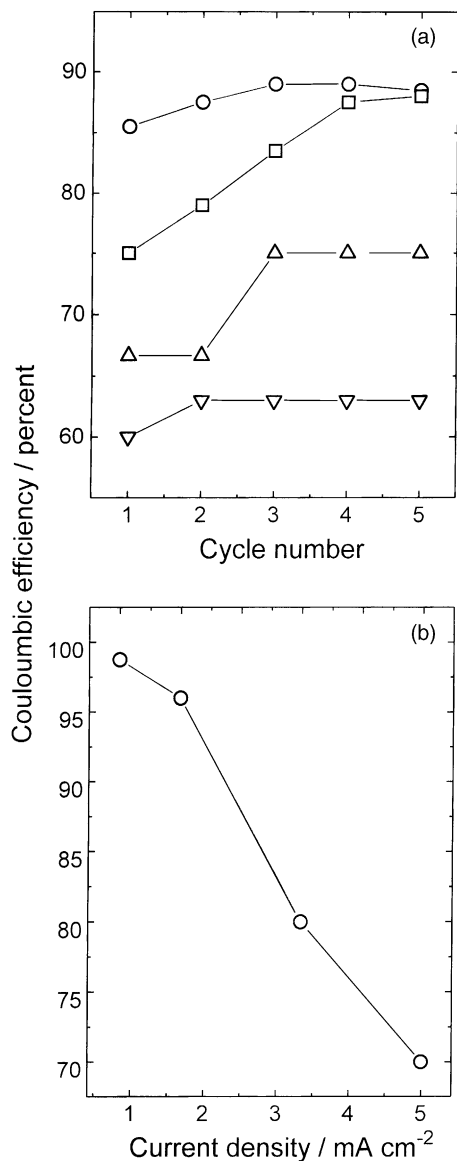


Fig. 7. Coulombic efficiency of anodic stripping of Li on Al surface (a) as function of cycle number at current density of (○) 0.83, (□) 1.66, (△) 3.33, and (▽) 5.0 mA cm⁻² and; (b) as function of current density. Data in (b) correspond to fifth cycle.

potential during the charge–discharge cycle is shown in Fig. 6. The electrode was subjected to several cycles and the coulombic efficiency of discharge is shown as a function of cycle number in Fig. 7. At a current density of 0.83 mA cm⁻², the efficiency is about 85% for the first cycle, and increases to and remains at 90% from the third cycle onwards. It is noteworthy that the deposition of Li during charging is always uniform and free from dendrites over several cycles.

It is generally believed that the development of rechargeable Li batteries has been hampered by the dendritic and spongy deposition of Li on the Li substrate during charge–discharge cycling. This problem has led to the development of a carbon-based negative electrode which allows reversible

intercalation–de-intercalation of Li within its layers. The capacity of carbon, however, is about 340 mAh g⁻¹ (corresponding to the composition C₆Li) which is considerably <3.8 Ah g⁻¹ of pure Li metal. In order to utilise the high-capacity Li metal as the negative electrode for rechargeable batteries, attempts have been made to reduce the dendritic deposition [12–15]. Dendrite-free deposition of Li on a Ni substrate in the presence of 5 mM HF in the electrolyte over repeated cycles has been reported [12]. The use of Li–Al alloy instead of pure Li has also been studied [13,14]. In a recent study [15], Al films of thickness in the range 0.1–1 μm have been deposited by thermal evaporation on copper substrates and evaluated as negative electrodes for Li-ion cells. In the present study, the deposition of Li on Al foil electrodes is found to be free from dendrites during several cycles which shows that Al can be used as the negative electrode in rechargeable Li batteries.

An Al electrode was removed from the cell after several cycles, washed with water for oxidation of any Li present on the surface, and dried. The electrode still remains grey which suggests that the colour is not due to metallic Li on the Al surface, but to Li which has penetrated into Al and caused the formation of Li–Al alloy. This was confirmed by comparing the XRD patterns of unused Al and grey Al specimens (Fig. 8). The XRD pattern of the Al specimen (Fig. 8(a)) matches the standard pattern of Al. There are, however, additional peaks at 2θ values of 24.2, 40.1, 47.5,

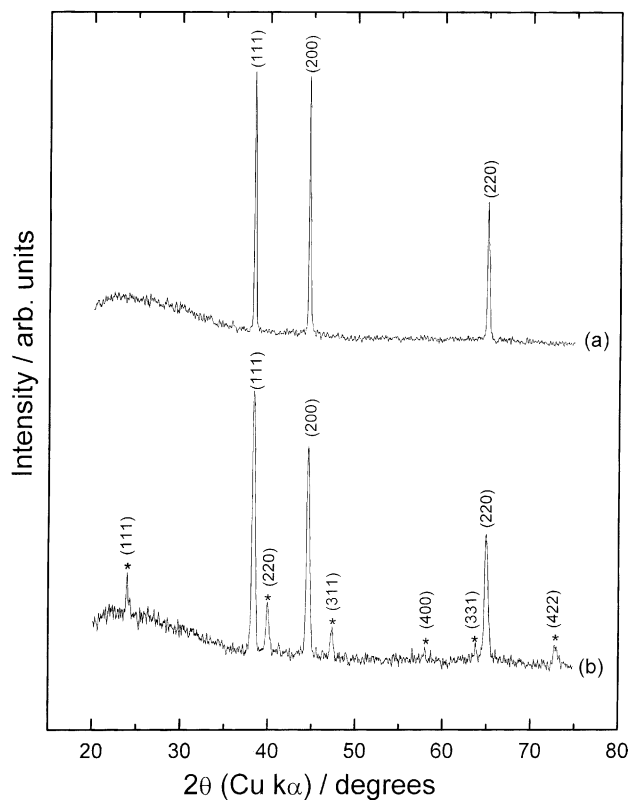


Fig. 8. XRD patterns for (a) Al (b) Li–Al alloy. Reflections marked (*) Li–Al alloy.

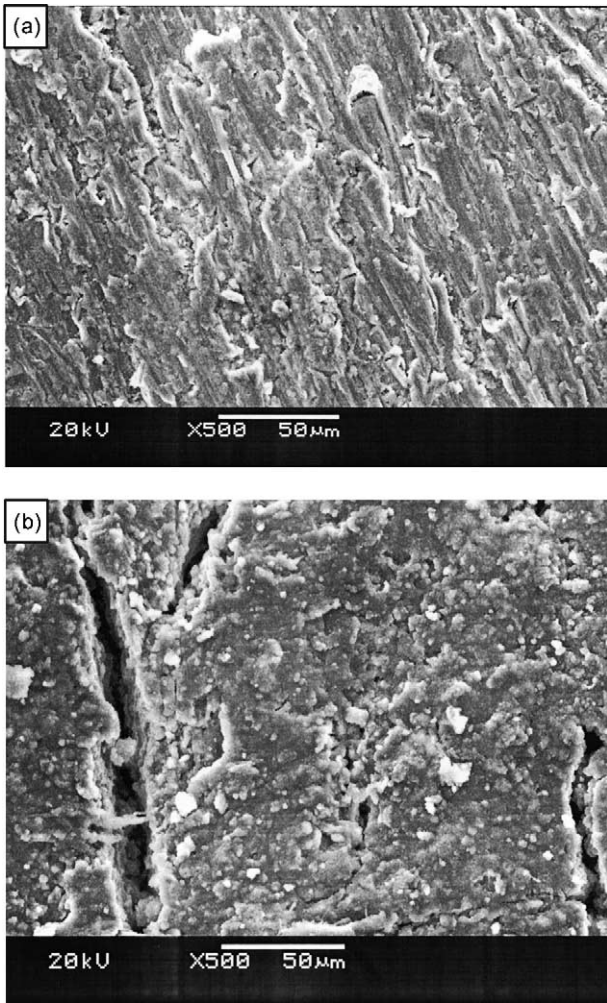


Fig. 9. Scanning electron micrographs of (a) pure Al foil (b) Li–Al alloy.

58.1, 63.8 and 72.9° in Fig. 8(b) which correspond to the Li–Al composition. The surface of the Al specimen was examined with a scanning electron microscope (Fig. 9). The micro-cracks which are distributed uniformly over the entire surface (Fig. 9(b)) are due to stresses that develop on insertion of Li into Al and result in the formation of alloy. Micro-cracks of this type are absent in an unused Al specimen (Fig. 9(a)).

The electrodeposition of Li on Al, and its anodic oxidation processes, (reaction 2) was studied by Tafel and linear-polarisation techniques in stirred electrolytes. Typical data are shown in Fig. 10. The relationship between the current density (i) and the overpotential (η) for reaction (2) is given by:

$$i = i_0 \left(\exp\left(\frac{-\alpha F \eta}{RT}\right) - \exp\left(\frac{(1-\alpha) F \eta}{RT}\right) \right) \quad (3)$$

where i_0 is the exchange current density the energy-transfer coefficient α other symbols have their usual meanings. The cathodic and anodic Tafel regions are linear with slopes of about 0.27 V decade⁻¹ Thus, the average value of α becomes

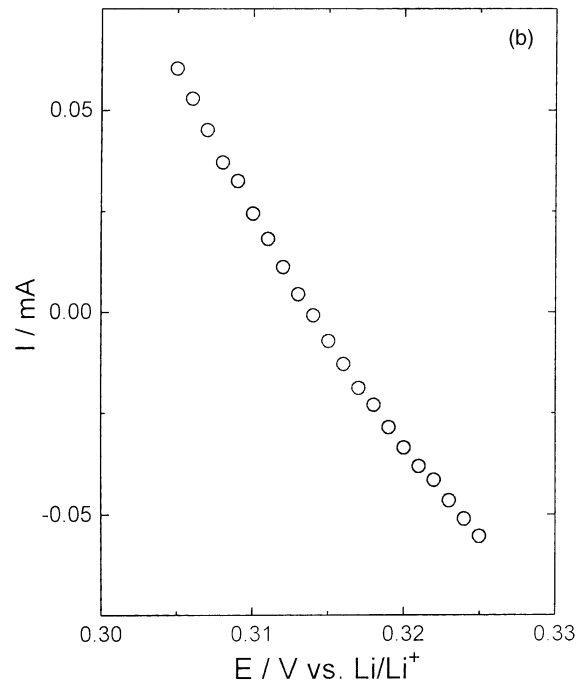
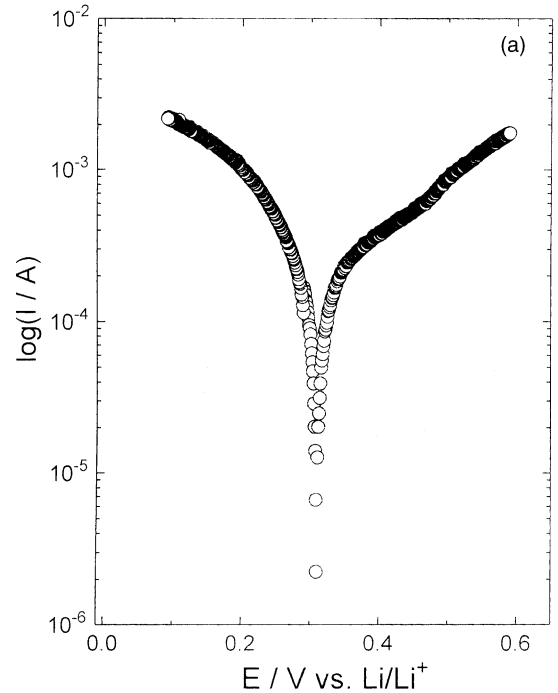


Fig. 10. (a) Tafel, (b) linear-polarisation curves for Al electrode (area = 1.2 cm²) in 1 M LiClO₄ in propylene carbonate electrolyte.

0.22 and suggests that reaction (5) is quasi-reversible. The value i_0 obtained by extrapolation of the Tafel region to $\eta = 0$ is about 0.16 mA cm⁻². The slope of linear-polarisation data (Fig. 10(b)) also provides i through:

$$\frac{d\eta}{(di)_{\eta=0}} = \frac{RT}{i_0 F} \quad (4)$$

Eq. (4) is obtained from Eq. (3) by linearizing exponential terms at low values of η . The value of i_0 evaluated from the data of Fig. 10(b) is 0.14 mA cm^{-2} , which is close to the value obtained from Tafel data. The above results support the suitability of Al as the negative electrode in non-aqueous Li batteries.

4. Conclusions

The electrochemical behaviour of Al in LiClO_4 -propylene carbonate electrolyte is studied by cyclic voltammetry, steady-state polarisation and ac impedance spectroscopy over the potential range -0.4 – 4.2 V versus Li/Li^+ . In the positive potential region Al is fairly stable between 1.57 and 3.5 V owing to the presence of a surface film. Nevertheless, oxidation of Al occurs at potentials $>3.5 \text{ V}$. From ac impedance measurements, the value for the surface film resistance is found to be between 498 and $1032 \text{ k}\Omega \text{ cm}^{-2}$. In the potential range from 3.6 to 4.2 V , there is breakdown of the passive film which results in a decrease in its resistance to 1.2 – $48 \text{ k}\Omega \text{ cm}^{-2}$. In the negative potential region, the deposition of uniform and non-dendritic Li occurs. This deposit can be anodically stripped in a quasi-reversible process with high coulombic efficiency. Diffusion of Li into Al results in the formation of a surface layer of Li–Al alloy. The quasi-reversible, dendrite-free, cathodic deposition and anodic stripping of Li with an exchange current density of 0.16 mA cm^{-2} suggests that Al may be useful as negative electrode for Li batteries.

Acknowledgements

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