

Electrolytes and additives for high efficiency lithium cycling

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Abstract

The use of lithium metal in rechargeable batteries continues to be of interest because only lithium metal can provide the very high energy density required in some specialist applications. However, major improvements are required in cycling efficiency, leading to longer cycle life, and in plating morphology to avoid dendrite formation which can lead to cell short-circuiting and safety problems. In this work the lithium plating/stripping efficiency has been measured for a range of electrolyte compositions both with and without additives such as surfactants and complexing agents. This was done with cells in which lithium was plated from a lithium-metal foil counter electrode onto a stainless steel electrode. In other respects, the cells were designed to be similar to complete cells except for the absence of a cathode; the minimum quantity of electrolyte was used and contained within a thin separator and stack pressure was applied. Improvements in cycling efficiency were found for some of the electrolyte compositions particularly those containing certain additives, e.g. perfluoropolyethers and by the use of 1.6 bar stack pressure. The high efficiencies were correlated with constant potential profiles during galvanostatic charge and discharge.

Keywords: Electrolytes/non-aqueous; Lithium anodes

1. Introduction

Recent advances in secondary lithium battery technology have led to increasing demands for the use of lithium battery systems in high energy density applications [1]. Most of the cells in the market use lithium-carbon ('lithium-ion') electrodes to avoid problems with lithium plating though lithium-metal cells are still of commercial interest [2]. If lithium-metal cells could be cycled reliably and safely, they would provide the ultimate energy density; however the main problem which has hampered development is one of redistribution of the lithium-metal anode upon cycling, from a compact metal foil to a porous and dendritic structure. The reaction of these dendrites (facilitated by their high surface area) with electrolyte and impurities leads to corrosion and isolation of lithium and, consequently, a gradual loss in cycling capacity. In addition the presence of finely divided lithium presents safety problems, especially when a lithium-metal anode is used.

Active research on the lithium-metal anode is still being pursued in many research laboratories [2]. A majority of this

research is focussed on improving cycling efficiency and safety through modifying plating conditions. A number of different approaches have been adopted with varying degrees of success at modifying the morphology of the lithium deposits and improving cycling efficiency. These include:

- (i) the use of more inert solvent/solvent mixtures [3–6];
- (ii) developing and using novel electrolyte salts [4,7,8];
- (iii) increasing the stack pressure on the lithium-metal anode [9,10];
- (iv) the addition to the electrolyte of compounds which improve the plating morphology [11,12].

Previous work in this laboratory examined the morphology of the interface during charge and discharge [13,14] for a number of electrolyte/salt combinations.

This work investigated a wide range of electrolyte compositions, including additives for the improvement of plating morphology, using potentiometry to monitor the condition of the interface while measuring the plating/stripping efficiency. The effect of the different electrolytes was also investigated under the condition of stack pressure which had already been shown to improve the efficiency. Cells were designed to represent as realistically as possible the condi-

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tions inside a battery with a small ratio of electrolyte volume to lithium surface area and to include stack pressure.

2. Experimental

2.1. Materials

Propylene carbonate (Aldrich, 99%) (PC) was distilled under vacuum at 0.13 torr. Molten ethylene carbonate (Fluka, 99%) (EC) was vacuum dried at 38°C for 24 h. PC/EC solvent mixtures were prepared by mixing the separate solvents in the volume ratios corresponding to 50:50 vol./vol.%. LiAsF_6 (Lithco, electrochemical grade) and LiPF_6 (Aldrich, 98%, recrystallised from DME, Aldrich, 99.9%) were vacuum-dried at 90–120°C and dissolved in the solvents and solvent mixtures as required.

Perfluoropolyether, PFPE (Fluorochem, 99%) was used without further purification. Bis- $[\text{C}_5\text{H}_5\text{CON}(\text{CH}_2\text{CH}_2\text{OCH}_3)_2]\text{Fe}(\text{II})$ (additive 2) and bis- $[\text{C}_5\text{H}_4\text{CON}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]\text{Fe}(\text{II})$ (additive 3) were supplied by Dr Martin Grossel of the University of Southampton.

Preparation of all solutions was carried out in an Ar filled glove box. Lithium foil, 0.1 mm thick (Lithco), was used in all experiments.

2.2. Cells

Three-electrode cells as shown in Fig. 1(a) were used for chronoamperometric studies and the determination of plating/stripping efficiencies without stack pressure.

Two-electrode cells used for cycling studies under stack pressure conditions were based on the design shown in Fig.

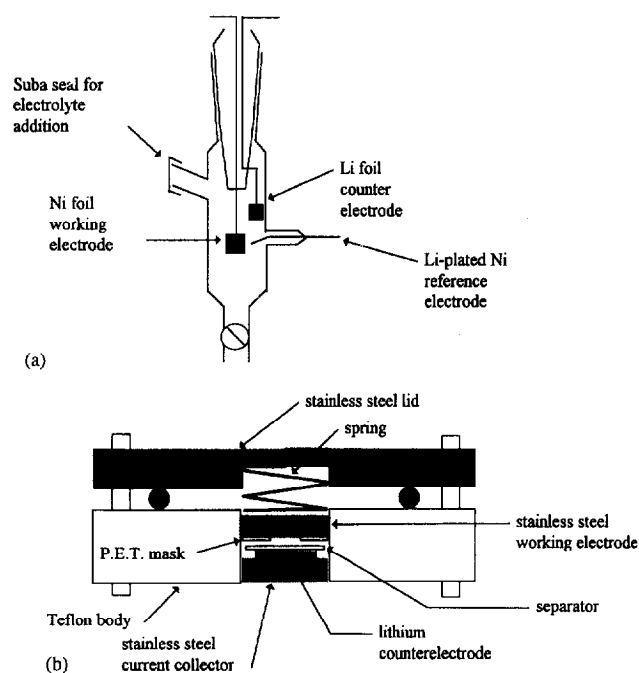


Fig. 1. Schematic designs for: (a) the three-electrode cell; (b) the stack-pressured cell.

1(b). The cell lid was a stainless steel disc and the cell body was fabricated from a cylindrical Teflon block. A hollow cylinder (diameter = 35.2 mm) in the main block housed both the working and counter/reference electrodes. The working electrode was a movable stainless steel disc which just fitted into the electrode housing, while a fixed stainless steel base acted as the counter electrode current collector. The working electrode area of 3.11 cm² was defined with a polyethylene terephthalate ring (Goodfellows, 0.005 mm thick) placed on the stainless steel surface. A lithium foil disc (area = 4.2 cm²) acted as counter electrode. Two Celgard 3501 separator discs (diameter = 35 mm) were placed between the working and counter electrodes to prevent direct electrical contact as well as to contain the electrolyte. A 50.8 mm stainless steel spring, with a force constant of 1.740 N mm⁻¹ which fitted loosely into the working electrode and a hollow in the cell lid acted as electrical contact between the working electrode and cell lid. Application of stack pressure to the working electrode was accomplished by screwing the lid to the cell body as shown, compressing the spring by about 80% of the free length to give a stack pressure of 1.6 bar on the working electrode.

2.3. Techniques and instrumentation

Cycling was achieved with a six-channel home built galvanostatic unit interfaced to a microcomputer. Each channel delivered constant currents (+ve and -ve) in the mA range within an accuracy of $\pm 0.1\%$ as measured by a Keithley digital multimeter.

Lithium was plated to about 1 μm thickness, equivalent to a capacity of $Q_P = 9 \text{ C cm}^{-2}$, and stripped galvanostatically from a nickel substrate at current densities ranging from 1 to 2.5 mA cm⁻². A relaxation period of 1800 s was allowed between plating and stripping half-cycles. The stripping capacity (Q_S) was determined by the amount of charge passed up to the point when the stripping potential increased to a cut-off potential of 1.0 V. The cycling efficiency per cycle, E_c , was determined by the ratio $Q_S/Q_P \times 100(\%)$.

3. Results and discussion

Fig. 2 shows potential profiles during many cycles of constant-current lithium plating onto nickel in the three-electrode cell without stack pressure for fixed periods followed by stripping to a fixed potential limit of 1.0 V. Differences in the plating/stripping profiles are shown for the two electrolytes, 1 M $\text{LiAsF}_6/\text{EC}/\text{PC}$ in Fig. 2(a) and 1 M LiAsF_6/PC in Fig. 2(b). These forms were found to be repeatable on further cycling.

The potentiograms may be analysed as follows. In both cases an initial negative potential peak is shown during the beginning of the plating cycle, representing the nucleation overpotential followed by the early stages of deposition of a lithium film. In the case of Fig. 2(a) this is followed by a

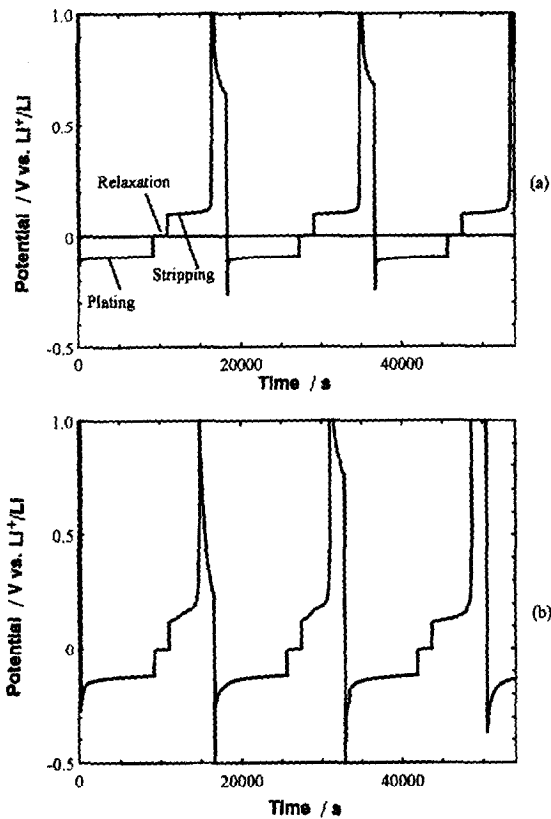


Fig. 2. Three-electrode chronopotentiograms for plating, relaxation and stripping in two contrasting electrolytes: (a) 1 M LiAsF₆/EC/PC; (b) 1 M LiPF₆/PC.

region of constant potential, consistent with a constant current density and thus a constant interfacial area throughout the plating process. On reversal of the current, almost the same constant potential is shown for most of the second half-cycle, with a reversed sign, suggesting that the interfacial area remains at a constant value. The final part of the cycle shows a very rapid rise in potential as final stripping of the film occurs uniformly over the entire surface. The situation is contrasted in Fig. 2(b) with a case where an initially high negative potential gradually falls, probably because of an increase in the surface area associated with dendrite formation. The stripping half-cycles generally show a potential increasing with time, probably because of a distribution of the lithium plate in various degrees of contact with the substrate.

A larger selection of chronopotentiograms is shown in Fig. 3 for 1 M LiPF₆/PC solution, with and without various additives in different concentrations. It may be seen that the potential profiles fall into either of the two classifications above. The plating potentiograms showing almost constant potential in Fig. 3(a) (open and closed circles correspond with the highest stripping efficiencies, around 80% as shown in Fig. 3(b)).

The high efficiencies were continued on further cycling, as confirmed by subsequent potential profiles (not shown) whereas experiments showing potential variations during early cycling soon led to electrode failure through unaccept-

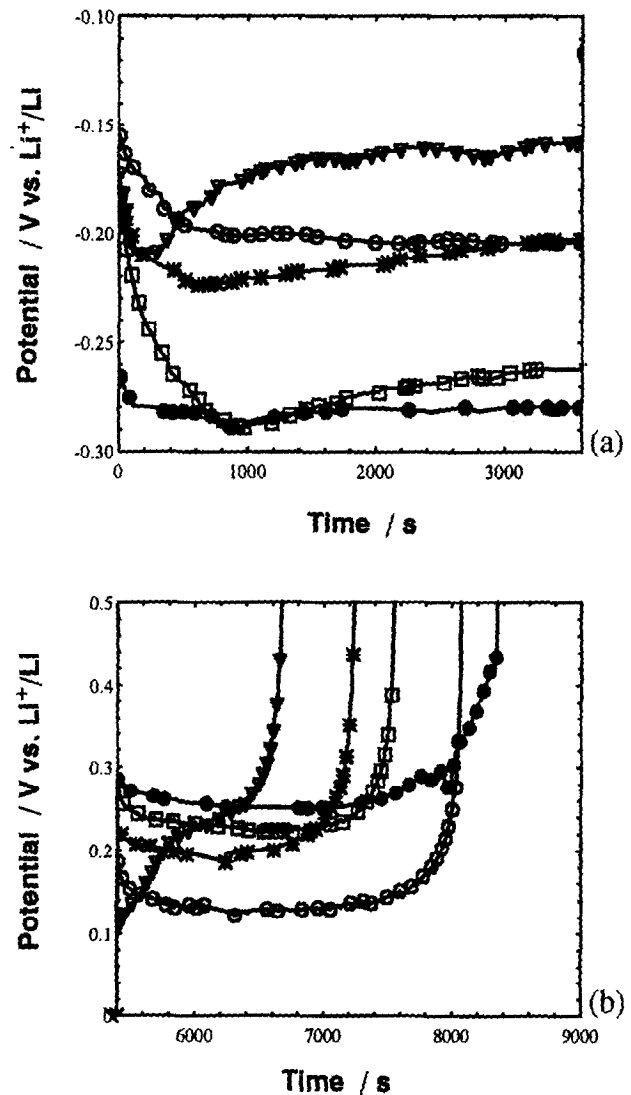


Fig. 3. Three-electrode chronopotentiograms for (a) plating and (b) stripping in various electrolytes: ●—● 1 M LiPF₆/PC/100 ppm PFPE; ○—○ 1 M LiPF₆/PC/30 ppm additive 3; *—* 1 M LiPF₆/PC; □—□ 1 M LiPF₆/PC/30 ppm additive 2; ▽—▽ 1 M LiPF₆/PC/200 ppm additive 2.

ably high plating and stripping potentials. It was therefore concluded that moderately high efficiencies and cell lifetimes could be predicted by the observation of constant potential during the first few plating half-cycles. The above analysis also confirmed that poor stripping efficiency originates from dendritic plating, and that the extent of the latter is a strong function of electrolyte composition. It would appear that additive 2 was only moderately effective in small concentrations, whereas additive 3 and PFPE gave substantial improvements in cycling of LiPF₆/PC solutions.

Potential measurements made during cycling under stack pressure are shown in Fig. 4 for the electrolyte LiAsF₆/EC/PC. Unfortunately, the profiles were distorted by the addition of overpotentials on the lithium counter electrode due to the two-electrode arrangement. For example, a peak is shown at the beginning of each stripping half-cycle because of the lithium plating overpotential on the counter electrode; also, the latter stages of plating half-cycles show increases due to

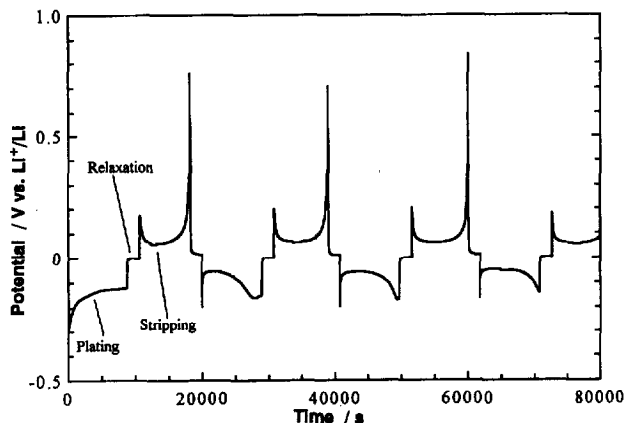


Fig. 4. Two-electrode chronopotentiograms for plating, relaxation and stripping in 1 M LiAsF₆/EC/PC under stack pressure.

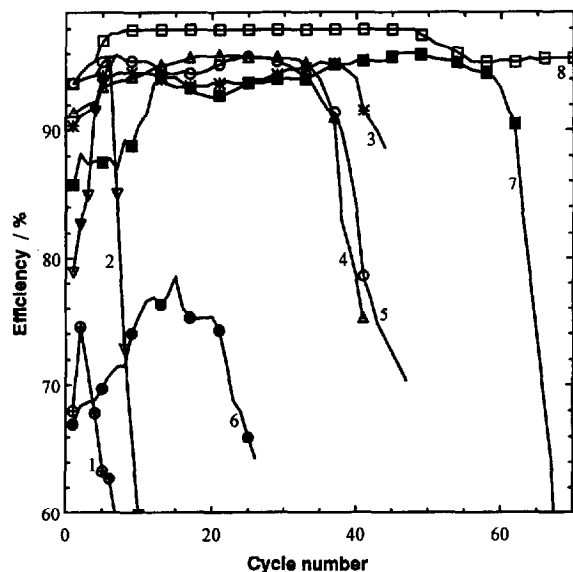


Fig. 5. Plating and stripping efficiency versus cycle number for various electrolytes: ⊕-⊕ (1) 1 M LiAsF₆/PC; ▽-▽ (2) 1 M LiAsF₆/PC/30 ppm additive 3; *-* (3) 1 M LiAsF₆/EC/PC/30 ppm additive 3; Δ-Δ (4) 1 M LiAsF₆/EC/PC/120 ppm additive 3; ○-○ (5) 1 M LiAsF₆/EC/PC; ●-● (6) 1 M LiAsF₆/EC/PC (no stack pressure); ■-■ (7) 1 M LiAsF₆/EC/PC/2000 ppm PFPE; □-□ (8) 1 M LiAsF₆/EC/PC/500 ppm PFPE.

counter electrode effects, obscuring any decrease in plating potential which could have been used to indicate an increase in interfacial area. However, it is clear that the stack pressure has led to a substantial increase in the plating/stripping efficiency in this case. It is suggested that the rising profile toward the end of stripping is due to a non-compact lithium which is only stripped under stack pressure conditions.

Fig. 5 shows the efficiency as a function of cycle number for two electrolytes 1 M LiAsF₆/EC/PC and 1 M LiAsF₆/PC with and without additives. The result for 1 M LiAsF₆/EC/PC without stack pressure is also given for comparison with the same electrolyte with stack pressure, showing a marked improvement. It was expected that solvent systems and additives which produced good results in free electrolyte

cells should give even better performance under stack pressure. Therefore the series of experiments was chosen to maximise the number of electrolyte compositions investigated and to seek high efficiency rather than to make direct correlations between the same electrolytes with and without stack pressure.

Common features in all the plots are an improvement with cycle number in the early stages, possibly due to the removal of reactive impurities from the electrolyte, a high efficiency plateau, and a final rapid degradation in most cases. As expected from the unfavourable potentiometric analysis and free electrolyte cycling results, the cell with the 1 M LiAsF₆/PC electrolyte under stack pressure showed an initially poor cycling efficiency and a deterioration over the first few cycles. Some improvement in cycling efficiencies was obtained in the presence of additives, the result shown for additive 3 (others being omitted for clarity) being a large initial improvement in the early stages followed by failure due to high resistance on extended cycling. This qualitatively confirms the potentiometric and free-electrolyte efficiency results noted for this additive when used with LiPF₆, although the quantitative result is disappointing.

The EC/PC electrolyte showed a marked improvement with stack pressure. Without additives the initial efficiency was around 90%, rising to a plateau at 94% before a final decline after 25–35 cycles. Additive 3 appeared to give a slight improvement at low concentration, where the curve shown represents the average of two experiments. However, the result was not confirmed at the higher concentration. In comparison, however, PFPE gave a marked improvement, with efficiencies around 94% sustained until cycle 60 in small concentration, whereas a larger concentration gave 98% efficiency for 48 cycles and 96% efficiency until the test was terminated at cycle 70. The cycling efficiency has thus been shown to be very sensitive to the composition of the electrolyte and much enhanced by stack pressure. In particular, EC/PC has been shown to give better cycling than PC, and the addition of mM concentrations of PFPE appears to have further enhanced the efficiency.

4. Conclusions

This work has shown that electrolytes and additives which improve lithium plating/stripping efficiency can be identified by constant potential regions during galvanostatic cycling. EC/PC has been shown to be superior to PC when used in conjunction with LiAsF₆. A perfluoropolyether additive has been found which further improves the efficiency. The improvements are further enhanced under stack pressure, where efficiencies above 95% were obtained. These results are particularly relevant to lithium battery technology because the experiments were performed for lithium plating/stripping in an environment close to that of a commercial lithium cell.

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