

Correlation between cycling efficiency and surface morphology of electrodeposited lithium.

Effect of fluorinated surface active additives

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Received 13 January 1995; revised 24 January 1996; accepted 9 February 1996

Abstract

The cycleability of a lithium anode has been investigated in two solutions containing LiClO_4 : (i) a propylene carbonate (PC) solution and (ii) a blended solution consisting of PC, ethylene carbonate (EC) and 1,2-dimethoxyethane (DME) (volume ratio = 1:1:2). Lithium and tetraethylammonium perfluorooctanesulfonate (LiFOS, TEAFOS) have been used as additives. Addition of these fluorinated surfactants at the optimum concentration, to electrolytic solutions, enhanced the lithium anode cycleability as the mean number of achieved cycles obtained is doubled in the presence LiFOS in PC and trebled (but with a larger dispersion) in the blended solution. The morphology of the lithium deposits has been observed by means of scanning electronic microscopy (SEM). SEM photographs of the lithium surface indicate that lithium deposited mainly as needle-like dendrites in PC- LiClO_4 solutions and as a metallic sponge in the blended solvent. In the presence of the additives, the structure of electrochemically deposited lithium is modified and appears to be less porous due to an enhanced and more uniform nucleation. After a few cycles, modifications of the morphology of the lithium deposit are visible and correspond, in both electrolytic solutions, to a smoother surface with occasionally large cracks. The cycle efficiency appears to be related to the morphological properties of the lithium surface. The use of the surface-active additives LiFOS and TEAFOS that compete with the solvents to form more compact and uniform surface films on lithium, improves the cycling efficiency.

Keywords: Cycling efficiency; Surface morphology; Lithium; Fluorinated compounds

1. Introduction

The cycle life of lithium (Li) secondary batteries is limited by the lack of reversibility of the Li anode which is mainly linked to the morphology of the electrodeposited Li. The formation of dendrites usually occurs during the plating period. Freshly deposited dendrites of Li are much more sensitive to a chemical attack by the electrolyte than a bulk piece of metal as the surface to volume ratio is very large. As a result, some dendrites become electronically isolated from the electrode surface [1]. Thus chemically active but electrochemically inactive 'dead lithium' reduces drastically the cycle life of the electrode [2]. Nevertheless, the conductive film formed at the metal–interface [3] is usually protective as it reduces the accessibility of the solvent to the metallic surface. It has been proved that the surface film (or solid electrolyte interface) mainly controls the behaviour of Li electrodes [4,5].

Rechargeable batteries that use Li intercalation compounds for the negative electrode provide, actually, the best compromise between large specific capacity and reversible cycling behaviour. However, a price is paid in terms of energy density and, to a lesser extent, in average output voltage as compared with an Li metal anode cell. Several research groups have tried to improve the reversibility of the Li electrode by the use of additives to the electrolyte solutions [6–12]. As a matter of fact, investigation concerning the role of additives to the electrolyte is not as popular today as it was ten years ago. However, the search for an additive that will produce improvement in Li-cycling efficiency is still going on. Recently, a paper was published concerning the use of a cationic surfactant [13]. In this paper, it is claimed that surfactants like tetraalkylammonium compounds with long *n*-alkyl groups increase Li-cycling efficiency. For cetyltrimethylammonium (CTAC) for example, the figure-of-merit (FOM) was 1.5 times the FOM for the additive-free

LiAsF₆-EC/2MeTHF (EC: ethylene carbonate, THF: tetrahydrofuran) electrolyte. The application of a stack pressure to the cell leads to a further increase in FOM but less than expected. At 125 kg/cm² the FOM was only 1.8 times the FOM under no pressure. This was attributed to the CTAC coverage on the Li surface which increases the contact resistance between the Li particles and the Li anode.

This paper describes the effects of anionic fluorinated surface-active agents on half-cell cycling efficiencies and Li morphology. The surfactants tetraethylammonium hepta-decafluorooctanesulfonate (TEAFOS) and lithium hepta-decafluorooctanesulfonate (LiFOS) have been used as additives. The presence of the perfluorinated chain gives to TEAFOS and LiFOS uncommon properties as compared with their hydrogenated homologues such as: chemical inertness in aggressive media, thermal stability, high surface activity at a low level even in organic solvents and an enhanced solubility in dipolar aprotic media [14]. Preliminary results show that cycling efficiencies are higher in the presence of these additives [14]. Therefore, the influence of the nature and the concentration of the additive on the cycling properties of the electrode, has been systematically investigated. In order to understand the cycling results, the surface morphology of the Li electrode has been examined by scanning electron microscopy (SEM).

2. Experimental

2.1. Solvents and solutions

Two solvents were used: pure propylene carbonate (PC) and an optimized mixture composed of PC (25 v/o), ethylene carbonate (EC: 25 v/o) and 1,2-dimethoxyethane (DME: 50 v/o). The usefulness of solvent mixtures for secondary Li battery applications has been explored from the point of view of better solution conductivity and Li-cycling efficiency [12,15–17]. The optimized mixture was selected because of the dissociating power of the cyclic carbonate ($\epsilon = 65.1$ and 89.6 for PC and EC, respectively) and the low viscosity of the ether. In this mixture the conductivity of the salts is enhanced.

PC, EC were purchased from Fluka (purity >99%), and DME obtained from Aldrich Chemical Company (purity >99.9%). The water content of the solvents was checked by the Karl Fischer method. It was found that the water content of commercial PC and DME were 140–160 ppm and 700 ppm, respectively. DME was stored over molecular sieves before use. Dried LiClO₄ (Fluka, microselect >99%, H₂O <0.2%) was used as received. The water content of the electrolyte PC-LiClO₄ (1 M) and PC-EC-DME-LiClO₄ (1 M) was about 250 ppm. Duplicates of cycling experiments using distilled solvent (PC, water content 60 ppm) gave results lying between the confidence interval limits (95%). At this level, the impurities present in the solvents have little or no effect as compared to the additives.

Both surfactants used as additives are commercially available. LiFOS (C₈F₁₇SO₃Li, Atotech technical reagent) was twice recrystallized from acetone and its purity was checked by differential scanning calorimetry. TEAFOS (C₈F₁₇SO₃-(C₂H₅)₄N) was purchased from Fluka (purity >99%) and used as received.

The concentration of LiClO₄ was 1 M in all electrolyte solutions and these were prepared in a glove box under an argon atmosphere.

2.2. Electrochemical measurements

All experiments were carried out at 25 °C using a Tacussel (Model PJT 16-0.6) potentiostat/galvanostat. The total volume of the electrochemical cell was 50 mL. The reference electrode was placed in a separated compartment using a porous glass separator (Vycor frit). The counter electrode was made from a pure-Li metal rod (diameter: 10 mm, Parker). During the cycling experiments, the composition of the electrolyte did not vary as the electrolyte was in a large excess. The role of the compounds produced on the working electrode at high overpotential is therefore minimized and no influence of the proportion between the volume of electrolyte and the quantity of electrodeposited Li was expected.

All potentials referred to the Li⁺/Li couple in 1 M LiClO₄-PC. In a previous work [14], Li was plated on a titanium electrode and cycled at 100% depth-of-discharge (DOD) [12]. But it appears that the cycling results, obtained by this method, were dependent on the surface state of metal used as substrate. Thus, in order to minimize the influence of the nature of the metal substrate, Li-cycling experiments were done on an initial deposit of Li. The initial plating of Li on a nickel substrate ($Q_p = 6$ C/cm²) occurred galvanostatically at 1.25 mA/cm². After a rest period of a few minutes, stripping and plating operations were performed successively at a DOD of 25%. Stripping and plating ($Q_s = Q_d = 1.5$ C/cm²) were conducted at current densities of 5 and 1.25 mA/cm², respectively. Cycling was stopped when the oxidation potential reached 1.5 V versus Li⁺/Li; the number of efficient cycles, N , was recorded.

The Li-efficiency, E , was evaluated from N according to the following formula:

$$E = 1 - [(Q_p - Q_s) / (Q_p N)]$$

All experiments were run at least in triplicate. The reproducibility of the experiments was evaluated by calculating the confidence interval for a 95%-confidence level. Additional experiments (usually four to six) were carried out when the standard deviation for N was larger than 1.5. Only the mean value \bar{N} and the corresponding value for E is reported in Table 1.

The electrolyte was used as soon as prepared. Storage over a large Li surface (the counter electrode) for a long time might have a pronounced effect on the water content and on the subsequent cycling experiments.

Table 1
Results of half-cell cycling in 1 M LiClO₄-PC (I) and 1 M LiClO₄-PC/
EC/DME (II)

Electrolyte	Additive	\bar{N} ^a	Precision ^b	E (%) ^c
(I)		18.3	± 3.2	83
(I)	TEAClO ₄ (0.01 and 0.025 M)	18.8	± 3.8	84
(I)	LiFOS (0.02 M)	11.0	± 3.2	71
(I)	LiFOS (0.01 M)	35.5	± 4.16	91
(I)	LiFOS (0.005 M)	26	± 5.5	88
(I)	TEAFOS (0.025 M)	21.8	± 3.15	86
(II)		13.5	± 4.2	75
(II)	LiFOS (0.05 M)	10.8	± 2.5	71
(II)	LiFOS (0.025 M)	12.0	± 3.2	74
(II)	TEAFOS (0.05 M)	17.4	± 3.3	82
(II)	TEAFOS (0.025 M)	41.7	± 6.4	93
(II)	TEAFOS (0.01 M)	12.8	± 1.4	77

^a Number of achieved cycles (mean).

^b Confidence interval for \bar{N} with a 95%-confidence level.

^c E (%) = $100[1 - (Q_p - Q_c)/(Q_c \bar{N})]$.

2.3. Scanning electron microscopy

For microscopic observation, Li was deposited electrochemically onto a coin of pure Li (diameter: 5 mm, thickness: 2 mm), obtained by crushing a piece of Li between two titanium rods in a Teflon holder. Pure Li has been chosen as a metal substrate in order avoid any possible influence of a foreign metal on the structure of the deposit. Moreover, these operating conditions are closer to real cycling conditions occurring in Li batteries. As described above, cycling experiments were conducted galvanostatically with a DOD of 25% (of the electrochemical deposit). In the glove box, the Li plate was washed with pure DME and made dry before its introduction into a sealed test tube filled with argon. The transfer of samples from the glove box to the microscope chamber was done in a manner so as to minimize exposure to atmospheric contaminants. A brief air contact was unavoidable during the transfer of the sample to the microscope chamber. Nevertheless, no effect of air moisture has been noted the time of contact was less than a few tenths of a second and the atmosphere of the laboratory was reasonably dry.

The electron microscope was a JEOL JEM 100CXII equipped with a scanning ASID 4D module.

3. Results and discussion

3.1. Lithium-cycling efficiency

In the absence of any additive, the mean value for \bar{N} was 18.3 and 14 for the PC-based electrolyte (I) and the optimized mixture (II), respectively. The corresponding half-cell cycling efficiencies, E , were 83% (I) and 75% (II). The influence of the additives TEAFOS and LiFOS on the cycling results has been investigated as a function of their concentra-

tion in the two electrolyte solutions. The average number of efficient cycles \bar{N} , the limit interval at 95%-confidence level and the corresponding efficiency E are summarized in Table 1.

In the PC-based electrolyte, solutions containing LiFOS or TEAFOS exhibit an improvement in cycling efficiency but LiFOS is more efficient as \bar{N} is twice compared with the reference LiClO₄-PC solution. The cycling enhancement observed is of the same order of magnitude as that observed in the presence of the cationic surfactant, CTAC, in EC/2MeTHF-LiAsF₆ [13]. Like CTAC, LiFOS has a maximum efficiency at a concentration of 0.01 M beyond which the efficiency decreases. Any increase (> 0.02 M) or decrease (< 5 × 10⁻³ M) in the concentration of the additives results invariably in a decrease of the efficiency. At low concentrations, the film of surfactant adsorbed at the interface is in a gaseous state as proved by contact angle and surface tension measurements [14]. At a concentration of 0.01 M, the transition of the surface film from a gaseous state to a liquid expanded state is achieved and the protection of the metal from solvent attack is more efficient. At higher concentration, the formation of a multilayer film of surfactant probably occurs leading to an increase of the surface ohmic resistance and to the observed anodic and cathodic overvoltage. As a consequence Li plating becomes more difficult. The fluctuation limits are slightly larger in the presence of the additive at the optimum concentration (4.2 instead of 3.2). The use of TEAClO₄ as additive does not result in any increase in cycling performance. In the absence of the surface active anion FOS⁻, no cycling enhancement is expected.

In the optimized mixture (electrolyte II), a threefold increase in the average number of efficient cycles \bar{N} is observed at the optimum TEAFOS concentration (0.025 M). The optimum concentration for TEAFOS corresponds exactly to the minimum concentration required to obtain a saturation of the interface [14] without any overvoltage during the plating and stripping operations. Nevertheless, at the optimum concentration the observed fluctuation limits for \bar{N} are larger as the confidence interval is 6.4 instead of 2 to 3. It should be noted that any deviation from this optimum value gives rise to a sharp decrease in \bar{N} . In electrolyte (II) the surfactant LiFOS is ineffective, probably as a consequence of a different configuration in the adsorbed state.

The use of the additive TEAFOS in the optimized mixture leads to better results in the number of cycles achieved as compared with LiFOS in PC, but with larger fluctuations.

3.2. SEM observation of the surface morphology of electrodeposited lithium

Fig. 1 presents a picture of the bare surface of the uncontaminated Li substrate before any electrochemical deposition. Although the surface seems to be smooth to the naked eye, SEM observations reveal the existence of streaks and chips (40 μm in size) due to the imperfect sharpness of the scalpel edge used to cut the Li rod. As has been pointed out, see Refs.



Fig. 1. Surface of the uncontaminated Li substrate before any electrochemical treatment.

[18,19], before any electrochemical treatment, the Li substrate exhibits defects to a micrometer scale. These stripes and cracks will be the preferential locations of high current density [19] and dendrite nucleation.

Fig. 2 shows a typical SEM micrograph of electrodeposited Li from a LiClO_4 -PC solution (a) without additive and (b) with LiFOS. The deposit has been plated using the same conditions as previously stated but the metallic substrate used for SEM observations is a freshly cut Li rod.

In Fig. 2(a), Li has been mainly deposited in the shape of needle like dendrites of 4–5 μm in diameter and 20–30 μm in length. Also shown in this figure are the ‘bottlenecks’, narrow regions of the dendrites. As a lot of these narrow regions can easily disconnect them from the bulk, electronically isolated Li clusters are created leading to the formation of what is called ‘dead lithium’. This phenomenon is one of the prime causes of the low cycling efficiency of the Li anode.

In Fig. 2(b), in the presence of the additive LiFOS at a concentration of 0.01 M, the dendrites exhibit a fungoid growth with a thick tubular foot (10 μm in diameter) and a large cap at the top end (20–25 μm in diameter). At a larger magnification an array of hexagonal-shaped grains (with a diagonal length of about 3.5 μm) are visible on the surface of the caps. A schematic view of the dendrites formed in the absence or in the presence of the additive is shown in Fig. 3. As the dendrites are larger in the presence of the additive, a better filling of the void spaces in the deposit is achieved leading consequently to a less porous structure.

In the PC-EC-DME mixture, the morphology of the Li deposits is different as shown in Fig. 4(a) and (b), in the absence of any additive and in the presence of TEAFOS (0.025 M), respectively. The surface is far less dendritic and looks rather like that of a fretted metal. The grains, obtained in the presence of the additive and visible in Fig. 4(b), are

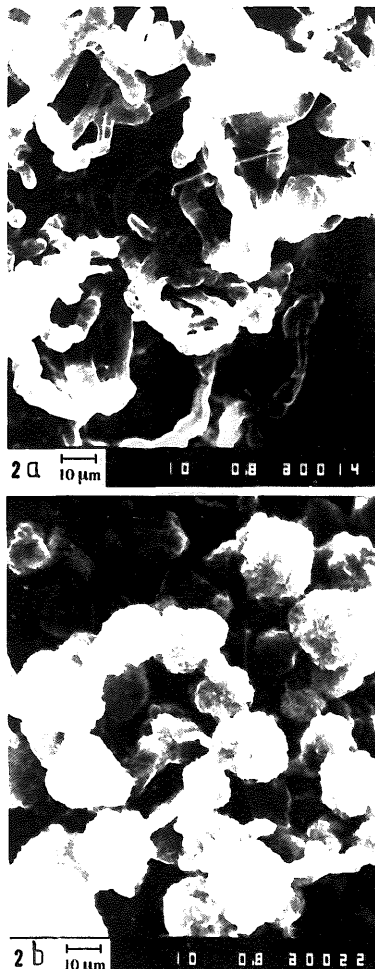


Fig. 2. Electrodeposited Li from a 1 M LiClO_4 -PC solution: (a) without any additives, and (b) with 0.01 M LiFOS as additive. Bottlenecks dendrites are clearly visible on micrograph (a).

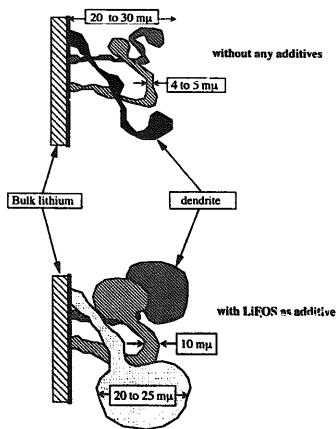


Fig. 3. Schematic view of Li dendrites formed by electrodeposition of Li on an Li substrate from a 1 M LiClO₄-PC solution: (top) without any additives, and (bottom) with 0.01 M LiFOS as additive.

of homogeneous dimension (mean edge: 10 μm) and present a uniform distribution. The pits separating the grains are about 10 μm in length.

It has been reported that the use of a mixture of PC + others, like DME or THF, increased Li-cycling efficiency as compared with pure solvents [20]. Nevertheless these results are controversial as another research group found that Li-cycling

efficiency deteriorates in PC + ether mixtures [17]. As a matter of fact, better cycling results are obtained in electrolyte (II) only in the presence of the additive TEAFOS.

3.3. SEM observation of the surface morphology of electrodeposited lithium after cycling

The treatment of the electrodeposited Li included five discharges and four charge cycles and the micrographs obtained are reported in Fig. 5. As shown in Fig. 5(a) and (b), for the PC-based electrolyte, the dissolution process leads to a destruction of the needle-like dendrites obtained from PC solutions. More generally, successive stripping and plating operations lead to the formation of a chaotic surface with a metal-sponge aspect.

In a PC medium and in the absence of any additive, the grains (10–15 μm) visible in Fig. 5(a) are distributed along the stripes of the Li substrate observed in Fig. 1. In the presence of LiFOS, the grains visible in Fig. 5(b) are slightly larger (20–30 μm) but more uniformly distributed. As a consequence, the orientation of the particles along the substrate's stripes is no longer visible. The presence of the additive adsorbed on the surface of the Li substrate leads to a more uniform distribution of the current density and the nucleation sites. These observations can be correlated with the improvement of the cycling efficiency.

The morphology of the Li deposits, obtained in the blended solvent after cycling in the presence or the absence of the additive TEAFOS, are visible in Fig. 6(a) and (b). After this electrochemical treatment and in the absence of the surfactant, the pits are more numerous and an uneven underlayer is

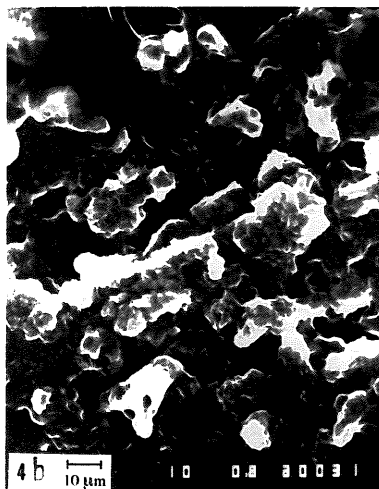


Fig. 4. Electrodeposited Li from a 1 M LiClO₄-(PC-EC-DME) (1:1:2) solution: (a) without any additives, and (b) with 0.025 M TEAFOS as additive.

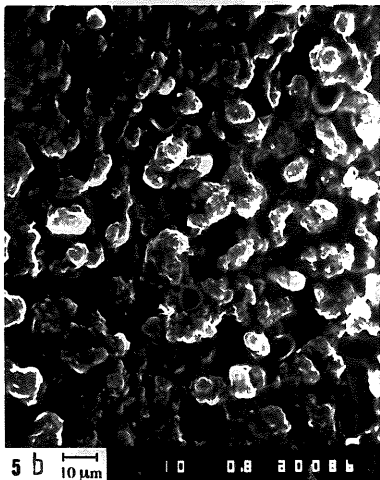
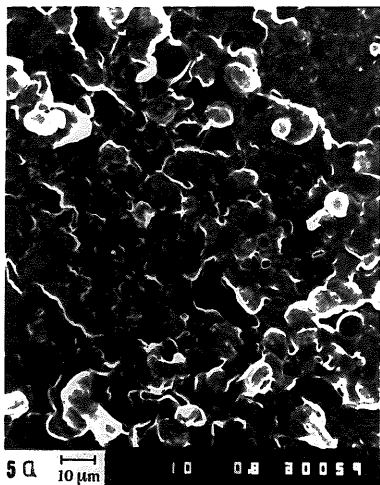


Fig. 5. Same conditions as in Fig. 2 but after five cycles: (a) without any additives, and (b) with 0.01 M LiFOS as additive.

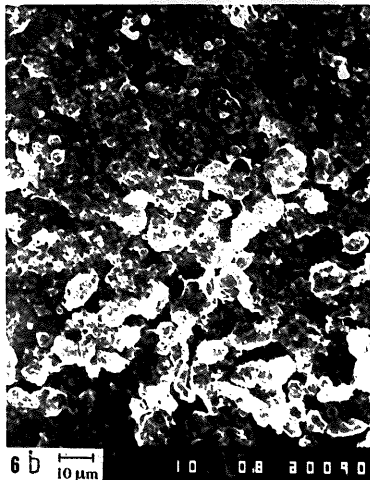
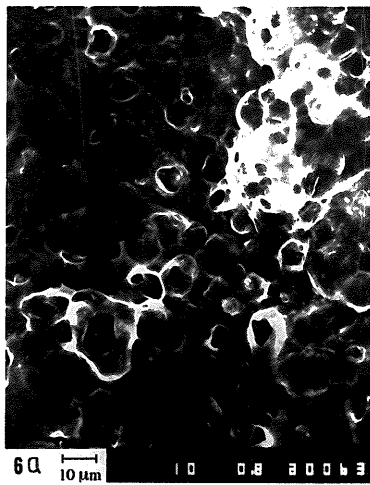


Fig. 6. Same conditions as in Fig. 4 but after five cycles: (a) without any additives, and (b) with 0.025 M TEAFOS as additive.

visible as compared with Fig. 4(a). As pointed out by others [2], Li is preferentially deposited and stripped at the side and the edges of the pits. The resulting deposit is highly porous as proved by its metal-sponge aspect.

The micrograph reported in Fig. 6(b) has been obtained in the presence of TEAFOS (0.025 M). In spite of an apparent

decrease in particle density, the surface morphology is not very different from that observed in Fig. 4(b). The structure obtained is highly compact. Therefore, the alteration of the surface aspect after a few cycles is less in the presence of the additive.

4. Conclusions

Fluorosurfactants increased Li-cycling efficiency when added to $\text{LiClO}_4\text{-PC}$ electrolyte solutions. A maximum number of 35.5 (about 4) cycles was obtained for LiFOS at 0.01 M in PC as compared with 18.3 (about 3 cycles) for the additive-free solution. In the ether-blended solvent PC-EC-DME, the surfactant TEAFOS was more effective and gave 41.7 (about 6.4) cycles at 0.025 M (13.5 for the additive-free electrolyte).

The observed improvement in Li anode-cycling efficiency in the presence of additives appears to be correlated with the surface morphology. The increase in cycling efficiency is mainly due to (i) a less porous structure restricting the exposure of the Li surface to a chemical attack by the solvent; (ii) larger dendrites or particles of Li leading to a reduced intergranular corrosion, and (iii) greater nucleation density leading to a uniform distribution of the Li particles.

As a conclusion, this study confirms that enhanced Li-cycling efficiencies can be obtained using anionic perfluoroalkylsulfonate as well as cationic tetraalkylammonium surface active additives. The positive effects observed at the Li anode in a flooded cell are an indication that these additives could be effective when tested in real cells.

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