

Reactivity and cycling behaviour of lithium in propylene carbonate–ethylene carbonate–dimethyl carbonate mixtures

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Received 27 October 1994; in revised form 12 January 1995; accepted 13 January 1995

Abstract

Lithium reactivity was investigated in a propylene carbonate–ethylene carbonate–dimethylcarbonate (1:1:3 volume) mixture with $\text{CF}_3\text{SO}_3\text{Li}$ and LiAsF_6 as the lithium salts. Resistance changes due to passivating layer formed on bulk lithium and electrodeposited lithium consumption were found to be diffusion-limited processes. Results indicate that lithium reactivity increases with the temperature. Moreover, it was shown that the addition of ethylene carbonate to propylene carbonate generally deteriorates both the lithium stability and the cycling characteristics, while the addition of dimethyl carbonate enhances these parameters.

Keywords: Lithium batteries; Organic solvents; Propylene carbonate; Ethylene carbonate; Dimethyl carbonate

1. Introduction

One of the major problems in the development of ambient temperature rechargeable lithium batteries is the insufficient coulombic efficiency of the lithium negative electrodes in organic electrolytes [1–3]. It is generally recognized that the composition of the electrolyte solution affects the lithium charge/discharge characteristics. Thus, many combinations of lithium salt/organic solvent have been examined as the electrolytes for practical rechargeable lithium batteries [4].

Alkyl carbonates are among the most important solvents for lithium batteries because they are polar, non volatile and non toxic but they are reactive towards lithium. So, many R&D groups have tried to improve lithium-cycling efficiency by the use of solvent mixtures containing an alkyl carbonate and an ether (5,6). Aurbach and Gofer [7] showed that lithium-cycling efficiency deteriorates in a mixture of propylene carbonate (PC) and ether due to the more complicated nature of the surface film formed on lithium in these solvent mixtures.

Ethylene carbonate (EC) is often used as a PC co-solvent [9–11]. The results are controversial: in some experimental studies, a better lithium cycling were found with the EC addition while in others studies the lithium-cycling efficiency was lower in the PC–EC mixture. In previous work, we have found better lithium-cycling efficiencies in PC–EC–dimethyl carbonate (DMC) mix-

tures than in PC–EC–dimethoxycarbonate (DME) mixtures [12]. In order to confirm this better behaviour of lithium in the presence of DMC, we have studied the stability of bulk lithium and electrodeposited lithium in DMC-based electrolytes. The influence of the electrolyte composition on the lithium-cycling characteristics was also investigated.

2. Experimental

2.1. Materials

Lithium hexafluoroarsenate (LiAsF_6) (electrochemical grade from Lithco) was used as received. Lithium triflate ($\text{CF}_3\text{SO}_3\text{Li}$) (3M Corporation) was vacuum dried at 120 °C for 24 h. PC from Fluka (high purity solvent > 99%), EC (purity > 99%) and DMC (purity > 99%) from Merck were used with no further purification.

Mixtures of solvents (their composition in volume of solvents will be given later) were prepared in a glove box and were stored over molecule 4A sieves that were previously vacuum activated at 250 °C. Lithium salts (1 M) were then added after the molecular sieves were taken off. The water content of each electrolyte was measured using a Karl Fischer apparatus and the conductivity was determined using a Tacussel conductimeter CDRV 62.

The analyses were performed in a glove box under an argon atmosphere at room temperature. Argon was regenerated by circulation through activated molecular 4A sieves.

2.2. Electrochemical investigations

The working electrodes were obtained by pressing a lithium rod into glass tubes. Their surfaces were cut just before immersion into the electrolyte, giving a clean metallic aspect surface (area: 0.285 cm^2). The counter electrodes for cycling were prepared in the same manner as the working ones. A piece of nickel sponge was used as the counter electrode for impedance measurements because of its high specific area. The reference electrode was a freshly cut lithium string directly immersed into the electrolyte.

Impedance measurements were performed using a computer controlled EG&G potentiostat (PAR 273). Impedance measurements were performed at an equilibrium potential of the system (0 V versus Li^+/Li) with a Schlumberger frequency analyser. The superimposed a.c. voltage was 5 mV and the frequency was scanned from 10^5 to 0.005 Hz.

Cycling was galvanostatically achieved using a computer-controlled IMT Tacussel interface and a Tacussel potentiostat.

3. Results and discussion

3.1. Stability of bulk lithium in PC-EC-DMC (1:1:3) mixtures

The Nyquist plots relative to bulk lithium always exhibit a distorted semicircle in the high to medium frequency range and a beginning of a straight line in the low frequency range (Fig. 1(a)). Even if this semicircle is a sum of processes [13], we prefer to consider it as a single one and to follow only its increase versus immersion time in the electrolyte. The intercepts of the semicircle with the real axis allow the resistance values to be calculated. These values deduced from impedance plots are in same order of magnitude as those obtained from polarization measurements (slope of the voltammetric curves near the equilibrium potential of the Li/Li^+ system from which ohmic drop is subtracted).

As already reported for other electrolytes [14], the resistance increases with the immersion time in the electrolyte. This increase arises from the passivating layer formed on lithium during its immersion in the electrolyte: the active metal reacts with the electrolyte components and the resulting reduction products precipitate on the surface and form the passivating layer.

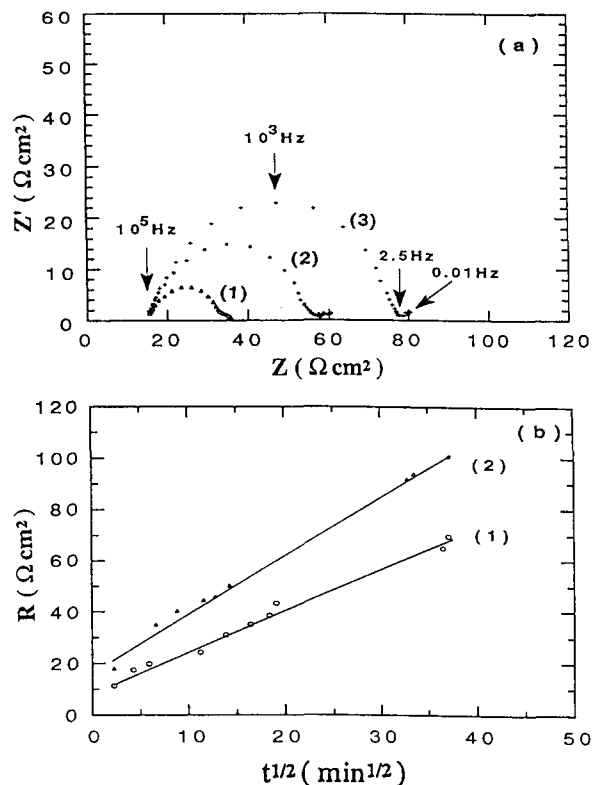


Fig. 1. (a) Impedance plots recorded at a lithium electrode in $\text{LiAsF}_6/\text{PC-EC-DMC}$ (1:1:3) mixture for different immersion times (t): (1) 20 min; (2) 5.5 h and (3) 22 h. (b) Resistance of a lithium electrode in PC-EC-DMC (1:1:3) mixture with (1) LiAsF_6 and (2) $\text{CF}_3\text{SO}_3\text{Li}$ salts vs. $t^{1/2}$.

Fig. 1(b) shows a linear relationship between the resistance and the square root of the immersion time in the electrolyte. Such a linear relationship, already reported for other electrolytes [15,16], indicates that the formation of the passivating layer is controlled by a diffusion process: either an electrolyte diffusion or an electron injection through the passivating layer are needed for the occurrence of the lithium/electrolyte reaction. Fig. 1(b) indicates that the increase in resistance depends on the lithium salt present in the electrolyte. This result is not surprising since the salt reduction products enter in the build-up of the passivating layer and/or lithium salts are embedded in the passivating layer (11–17).

3.2. Stability of electrodeposited lithium on bulk lithium in PC-EC-DMC (1:1:3) mixtures

Lithium is electrodeposited on bulk lithium under a current density of 1 mA cm^{-2} for a plating charge of 0.25 mAh cm^{-2} (Q_p). The deposit is left on open circuit for a controlled period of time, referred hereafter as 'storage time'. Stripping is performed under the same current density. All the electrochemically active lithium is assumed to be removed from the working electrode during the stripping procedure. As already

observed [12, 18], the stripping curve shows two components separated by a potential drop: the anodic component is attributed to the oxidation of electrodeposited lithium while the second component corresponds to the oxidation of bulk lithium. The faradaic efficiency (e) is calculated according to the relation:

$$e(\%) = (Q_s/Q_p) 100 \quad (1)$$

where Q_s is the stripping charge engaged during the less anodic stripping process.

Fig. 2(a) gives the change in the faradaic efficiency in PC-EC-DMC mixtures with LiAsF₆ and CF₃SO₃Li salts as a function of the storage time in the electrolyte. Initial efficiencies are lower than 100% due to lithium corrosion which simultaneously occurs with its electrodeposition. e also decreases during the storage because of reaction with the electrolyte: the greater the storage time, the more significant is the lithium consumption. Fig. 2(a) also indicates that the lithium corrosion decreases with the time due to the presence of a passivating layer on the metal.

Plots of $e-t^{1/2}$ are linear (Fig. 2(b)). Such plots agree well with the resistance changes reported earlier in this paper. Indeed, as far as the passivating layer growth is a diffusion-limited process, one may conclude that

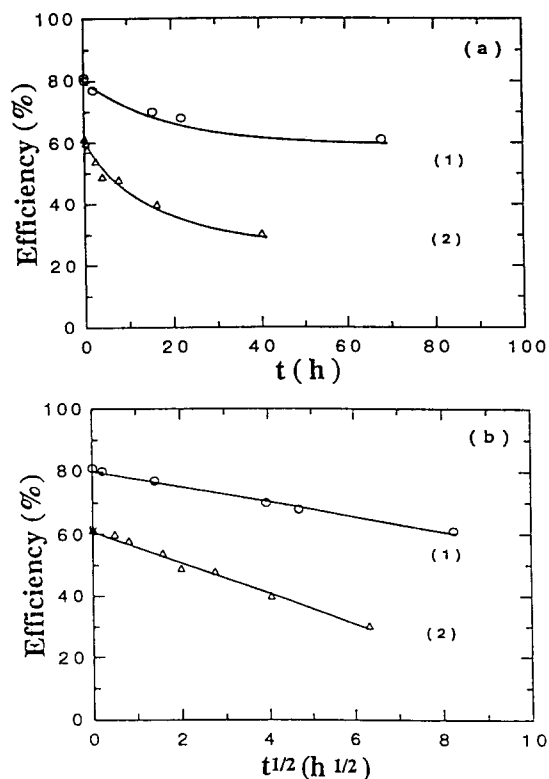


Fig. 2. (a) Efficiency vs. the immersion time (t) of electrodeposited lithium in PC-EC-DMC (1:1:3) mixture with (1) LiAsF₆ and (2) CF₃SO₃Li salts. (b) Efficiency vs. $t^{1/2}$ of electrodeposited lithium in PC-EC-DMC (1:1:3) mixture with (1) LiAsF₆ and (2) CF₃SO₃Li salts. Plating conditions on bulk lithium: $i=1 \text{ mA cm}^{-2}$; $Q=0.25 \text{ mAh cm}^{-2}$; stripping conditions: $i=1 \text{ mA cm}^{-2}$.

the lithium loss should obey a similar linear relationship, since the reduction products of the solvents and the lithium salt by lithium are the components of the passivating layer.

Fig. 2 shows that: (i) the initial efficiency is lower with CF₃SO₃Li salt than with LiAsF₆, and (ii) the slope of $e-t^{1/2}$ is lower with LiAsF₆ than with CF₃SO₃Li.

This confirms that the lithium salt intervenes in the formation of the passivating layer [11–17].

3.3. Influence of the temperature on lithium stability in PC-EC-DMC (1:1:3) mixtures

Conductivity evolutions of PC-EC-DMC mixtures (1:1:3) in the presence of LiAsF₆ and CF₃SO₃Li salts in the 25–53 °C temperature range are given in Table 1. This Table shows that the conductivity increase with temperature is more significant with LiAsF₆ than with CF₃SO₃Li.

Fig. 3(a) gives the resistance evolutions reported on bulk lithium at two temperatures during its immersion into the LiAsF₆/PC-EC-DMC mixture. Examination of this Figure indicates that the resistance values corresponding to the same immersion time in the electrolyte decrease with the temperature. In order to determine if this decrease is caused by an increase in conductivity or/and if the lithium reactivity is modified by the temperature, we have modified the temperature during storage (Fig. 3(b)). When the temperature is lowered at 23 °C after a storage at 53 °C for 2 h, the resistance values (curve (1) in Fig. 3(b)) are higher than those obtained during a storage only performed at 23 °C (curve (1) in Fig. 3(a)). But a return to 53 °C, after this transition to room temperature, allows us to obtain resistance values similar to those obtained during a storage performed at the temperature of 53 °C (curve (2)) in Fig. 3(a)).

On the other hand, resistance values obtained at 23 °C (curve (2) in Fig. 3(b)), after a transition at 53 °C, are higher than those obtained during a storage performed at ambient temperature (curve (1) in Fig. 3(b)).

Table 1

Conductivity vs. temperature of propylene carbonate–ethylene carbonate–dimethyl carbonate (1:1:3) mixtures with LiAsF₆ and CF₃SO₃Li salts

Electrolyte	Temperature (°C)	Conductivity (mS cm ⁻¹)
1 M LiAsF ₆ /PC-EC-DMC	23	10.1
	35	13.6
	44	17.1
	53	20.7
1 M CF ₃ SO ₃ Li/PC-EC-DMC	23	2.5
	40	3.1
	53	3.7

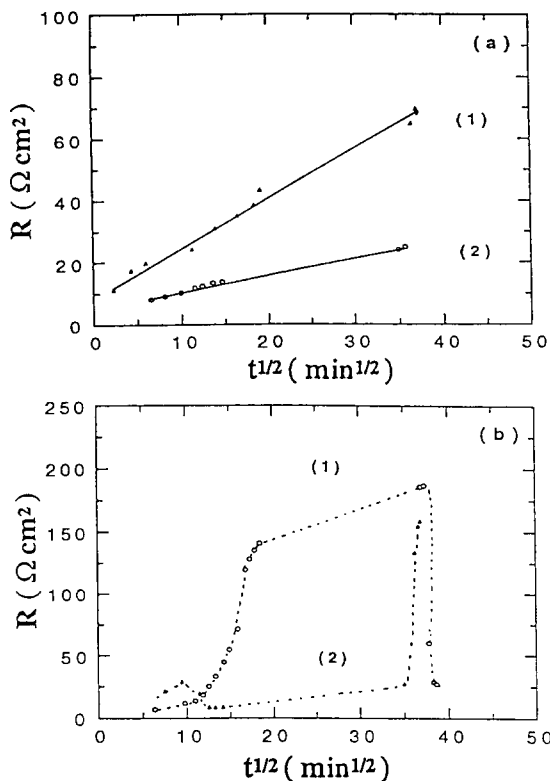


Fig. 3. Influence of temperature on resistance of bulk lithium electrodes: (a) stored at (1) 23 °C, and (2) at 53 °C; (b) (1) stored for 2 h at 53 °C, then at 23 °C for 15 h and finally at 53 °C, and (2) stored for 2 h at 23 °C, then at 53 °C for 15 h and finally at 23 °C. PC-EC-DMC (1:1:3) mixture and LiAsF_6 salt.

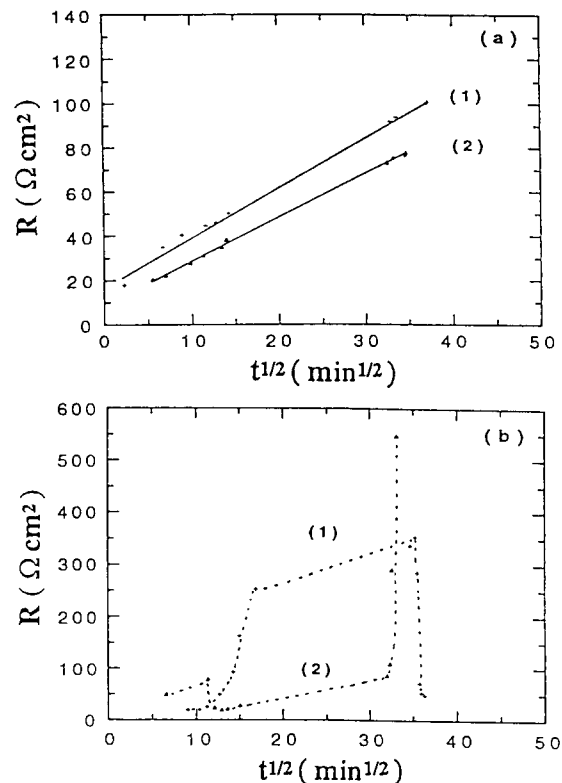


Fig. 4. Influence of temperature on resistance of bulk lithium electrodes: (a) (1) stored at 23 °C and (2) at 53 °C; (b) (1) stored for 2 h at 53 °C, then at 23 °C for 15 h and finally at 53 °C, and (2) stored for 2 h at 23 °C, then at 53 °C for 15 h and finally at 23 °C. PC-EC-DMC (1:1:3) mixture and $\text{CF}_3\text{SO}_3\text{Li}$ salt.

A similar behaviour of bulk lithium is obtained in $\text{CF}_3\text{SO}_3\text{Li}/\text{PC-EC-DMC}$ mixture (Figs. 4(a) and (b)).

These results suggest that temperature modifies not only the conductivities but also the magnitude of the reaction between lithium and the electrolyte as the resistance values are always higher after a transition at 53 °C. One can therefore conclude that the higher the temperature, the more significant is the lithium corrosion since resistance values are always higher after a transition at 53 °C.

Results obtained with electrodeposited lithium are in agreement with this conclusion (Fig. 5). With the LiAsF_6 electrolyte (Fig. 5(a)), the slope of the straight lines varies indicating that the rate of lithium corrosion is increasing with the temperature. With $\text{CF}_3\text{SO}_3\text{Li}$ electrolyte (Fig. 5(b)), the rate of corrosion does not change as significantly as with the LiAsF_6 electrolyte. This difference can be only attributed to the lithium salt since the solvents mixture is the same in both cases. So, one can conclude that the reaction, where the lithium salt intervenes, has a different activation energy depending on the salt used.

3.4. Influence of the mixture composition on lithium stability

Characteristics of the electrolyte mixtures investigated during this study are given in Table 2.

Stability of the electrodeposited lithium was analysed in these mixtures in the same way as that defined for PC-EC-DMC mixture, see Section 3.2.

Fig. 6 shows the stability of electrodeposited lithium in different mixtures as a function of the square root of immersion time. Initial efficiencies without storage time vary from 80 to 25% according to the nature of the solvents mixture and the lithium salt. Initial efficiencies may be considered as a good indicator of the electrodeposited lithium loss registered when lithium is continuously cycled. On the other hand, the slope of the straight lines expresses the reactivity of the electrodeposited lithium during its storage in the electrolyte. It allows an estimation of the lithium loss when lithium is submitted to sequences of cycling and storage. One may conclude according to Fig. 6 that the EC addition reduces either the stability of electrodeposited lithium or the initial efficiency, especially in the binary mixture. On the contrary, the presence of DMC tends to improve the stability of electrodeposited lithium, regardless the other solvents present in the mixture.

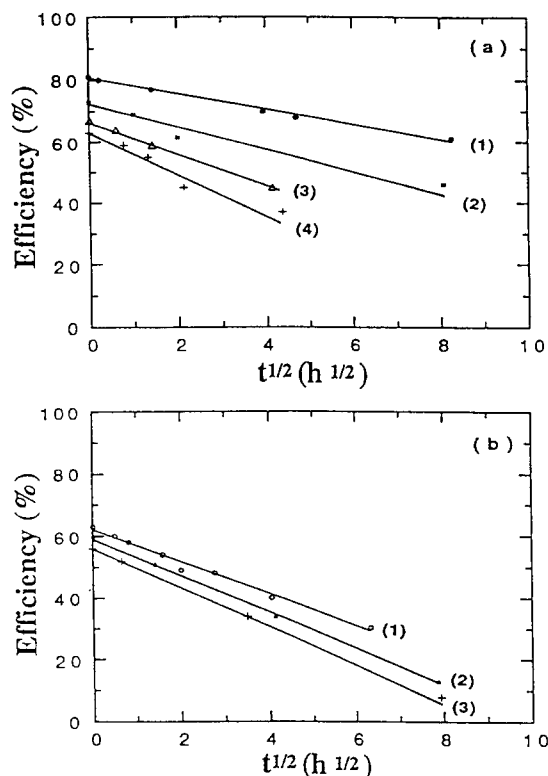


Fig. 5. Efficiency dependence of electrodeposited lithium with the temperature in PC-EC-DMC (1:1:3) mixture: (a) with LiAsF_6 : (1) 23 °C; (2) 35 °C; (3) 44 °C, and (4) 53 °C, and (b) with $\text{CF}_3\text{SO}_3\text{Li}$: (1) 23 °C; (2) 40 °C, and (3) 53 °C. Plating conditions on bulk lithium: $i = 1 \text{ mA cm}^{-2}$, $Q = 0.25 \text{ mAh cm}^{-2}$; stripping conditions: $i = 1 \text{ mA cm}^{-2}$.

Table 2
Conductivity and water content of different electrolytes at 25 °C *

Solvent mixture	Composition (vol. ratio)	Lithium salt (1 M)	Conductivity (mS cm^{-1})	Water content (ppm)
PC	1	LiAsF_6	5.42	60
PC	1	$\text{CF}_3\text{SO}_3\text{Li}$	1.75	50
DMC	1	LiAsF_6	7.75	50
PC-DMC	1:1	LiAsF_6	10.6	45
PC-DMC	1:1	$\text{CF}_3\text{SO}_3\text{Li}$	1.6	60
PC-EC	1:1	LiAsF_6	6.4	45
PC-EC	1:1	$\text{CF}_3\text{SO}_3\text{Li}$	2.7	50
EC-DMC	1:1	LiAsF_6	10.9	45
EC-DMC	1:1	$\text{CF}_3\text{SO}_3\text{Li}$	3.02	40
PC-EC-DMC	1:1:3	LiAsF_6	10.15	40
PC-EC-DMC	1:1:3	$\text{CF}_3\text{SO}_3\text{Li}$	2.56	50

* PC=propylene carbonate; EC=ethylene carbonate, and DMC=dimethyl carbonate.

3.5. Influence of the mixture composition on lithium-cycling behaviour

Cycling was achieved with lithium electrodes. The cycling-current density ($i_{\text{plating}} = i_{\text{stripping}}$) was 1 mA cm^{-2} and the corresponding cycling capacity was 0.25 mAh cm^{-2} (Q_n). No limitation of cycling occurs as far as

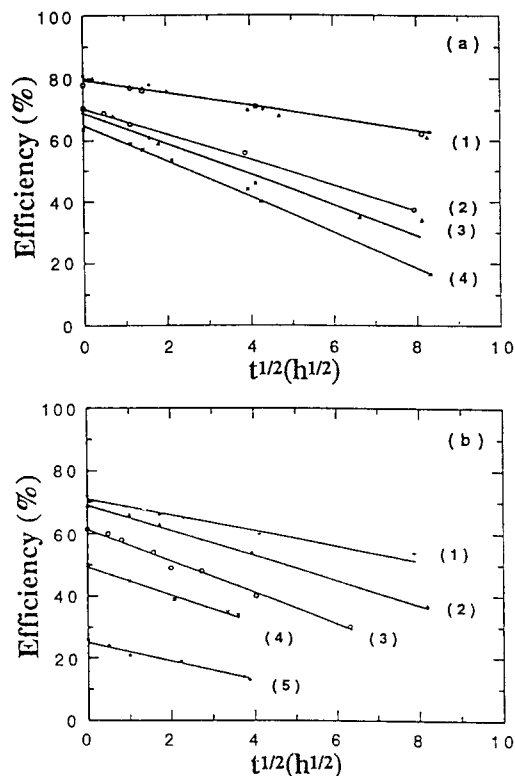


Fig. 6. (a) Efficiency vs. immersion time of electrodeposited lithium with LiAsF_6 : (1) DMC or PC-DMC (1:1) or PC-EC-DMC (1:1:3); (2) EC-DMC (1:1); (3) PC; and (4) PC-EC (1:1). (b) Efficiency vs. immersion time of electrodeposited lithium with $\text{CF}_3\text{SO}_3\text{Li}$: (1) PC-DMC (1:1); (2) PC; (3) PC-EC-DMC (1:1:3); (4) EC-DMC (1:1); and (5) PC-EC (1:1). Plating conditions on bulk lithium: $i = 1 \text{ mA cm}^{-2}$, $Q = 0.25 \text{ mAh cm}^{-2}$; stripping conditions: $i = 1 \text{ mA cm}^{-2}$.

the native lithium rod was not exhausted by the oxidation process in order to compensate for the loss of electrodeposited lithium.

The average efficiency (E) per cycle was calculated by the following equation:

$$E = (1 - Q_{\text{max}}/nQ_n) \quad (2)$$

where Q_{max} is arbitrary chosen as 1 mAh cm^{-2} and n is the cycle number when the sum of faradaic capacities engaged during the second component of the stripping curve reaches Q_{max} .

The figure-of-merit (FOM) was also calculated by the following equation:

$$FOM = 1/(1 - E) \quad (3)$$

FOM values obtained in different electrolytes are given in Table 3. This Table clearly shows that the best cycling behaviour is found in $\text{LiAsF}_6/\text{DMC}$ electrolyte. The addition of other alkyl carbonates induces a reversibility loss, in particular when EC is used. FOM values in EC-DMC mixtures are usually twice lower than those in PC-DMC mixtures. This is in agreement with results previously reported in Section 3.4. Moreover, Table 3 shows that better FOM values are obtained

Table 3
Figure-of-merit values obtained for lithium cycling in different electrolytes *

Solvent mixture	Lithium salt (1 M)	Figure-of-merit values
PC	LiAsF ₆	3.7
PC	CF ₃ SO ₃ Li	3.5
DMC	LiAsF ₆	13.7
PC–DMC	LiAsF ₆	8
PC–DMC	CF ₃ SO ₃ Li	4.2
PC–EC	LiAsF ₆	2.4
PC–EC	CF ₃ SO ₃ Li	1.4
EC–DMC	LiAsF ₆	3.2
EC–DMC	CF ₃ SO ₃ Li	2
PC–EC–DMC	LiAsF ₆	5.5
PC–EC–DMC	CF ₃ SO ₃ Li	3

* PC=propylene carbonate; EC=ethylene carbonate, and DMC=dimethyl carbonate.

with LiAsF₆ than with CF₃SO₃Li, regardless of the solvent mixture.

The efficiencies values are generally lower than those obtained in button cells. This is due to the experimental conditions chosen; those results are obtained on electrodes hanging freely in an excess of electrolyte and are not protected by separators as in button cells. However, the results of this study give a good estimation of the lithium reactivity and allow the selection of better electrolytes, which should be further tested in button cells for the development of rechargeable lithium batteries.

4. Conclusions

The results show that the structure of the alkyl carbonates strongly influences the lithium behaviour. In all electrolytes studied here, electrodeposited lithium consumption and bulk lithium stability are diffusion-limited processes suggesting that the decomposition products built up a passivating layer which hinders the

reaction between lithium and the electrolyte. Additional investigations are performed in our laboratory in order to better understand the influence of the alkyl carbonate.

Acknowledgements

This work was financially supported by the 'Direction des Recherches Etudes et Techniques' (DRET) under Contract No. 92 088.

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