

## Inorganic film-forming electrolyte additives improving the cycling behaviour of metallic lithium electrodes and the self-discharge of carbon-lithium electrodes

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### Abstract

The beneficial effect of some inorganic electrolyte additives like  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}$ -complexes and polysulfides  $\text{S}_x^{2-}$  on self-discharge and cycling behaviour of metallic lithium electrodes as well as of carbon-lithium intercalation electrodes is demonstrated in propylene carbonate (PC) electrolytes. Obviously, the above listed additives promote the formation of thin inorganic films on Li or  $\text{LiC}_m$ , respectively. Films of this kind, being permeable to unsolvated  $\text{Li}^+$  cations and almost impermeable to organic solvent molecules, are also formed in the absence of any additives, however, the additives seem to improve their quality and/or rate of formation. Impedance spectra indicate that the additives decrease in particular low frequency resistances. These low frequency resistances are apparently dominated by diffusion in pores, giving rise to curved Warburg branches. In view of the polymer electrolyte interphase (PEI) model the strong effect of the additives on the low frequency resistances may be related with smaller amounts of polymeric electrolyte decomposition products, i.e., thinner PEI layers. Although the chemical nature of the films formed in the presence of inorganic additives is still unknown, it may be concluded that a variety of material-different inorganic films is characterized by basically similar selective transport properties for  $\text{Li}^+$  ions and organic solvent molecules.

### Introduction

There have been considerable research activities in improving electrolyte systems for rechargeable lithium batteries by small amounts of additives. Most of the work reported so far deals with: (i) surface-active organic additives improving the morphology of deposited Li [e.g. refs. 1-3], and (ii) film-forming additives, supporting the formation of solid  $\text{Li}^+$  conducting films [e.g. ref. 4].

The most effective of the second group found so far is  $\text{CO}_2$  which drastically improves the cycling behaviour of metallic Li electrodes [5, 6].

This improvement is obviously related to the properties of the special films formed on Li surfaces in the presence of  $\text{CO}_2$ . As the protection of C-Li intercalation compounds in organic electrolytes is based on a quite similar mechanism [7],  $\text{CO}_2$  is also useful as an additive to reduce self-discharge of C-Li anodes [8]. As  $\text{CO}_2$  is quite

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sensitive to electrochemical reduction [e.g. ref. 9], it is to be expected that decomposition products of  $\text{CO}_2$  are incorporated in the films on metallic Li and C-Li intercalation compounds, respectively.

Unfortunately, the solubility of  $\text{CO}_2$  in common Li battery solvents is poor. Therefore, we were screening alternative inorganic additives which might have similar effects as  $\text{CO}_2$ , on the self-discharge of C-Li anodes and the cycling behaviour of metallic Li as well.

## Experimental

Capacity losses due to storage of  $\text{LiC}_n$  in the electrolyte solution were determined under standard conditions: charge and discharge at  $\pm 0.050$  mA/mg carbon, cut-off at 0.0/+2.0 V versus Li/Li<sup>+</sup> using the Amoco-Union Carbide pitch fibres P-100. Impedance studies were performed in the controlled current mode, using a Solartron 1174 frequency response analyser. Carbon fibre bundle electrodes were contacted with thin stainless-steel wires and placed in pyrex glass cells (large excess of electrolyte) with bulk Li counter electrodes. The cycling of metallic Li and the deposition of Li for morphological studies were performed in 'open' configuration without any separator and no force on Li. Standard cycling conditions were  $i_c = i_d = 1$  mA/cm<sup>2</sup> with  $Q = 2.7$  C/cm<sup>2</sup> on Li foil and Ni substrates.  $\text{S}_x^{2-}$  anions were prepared *in situ* by electrochemical reduction of an  $\text{S}_8$  electrode in the electrolyte solution.

## Results and discussion

### Lithium-carbon electrodes

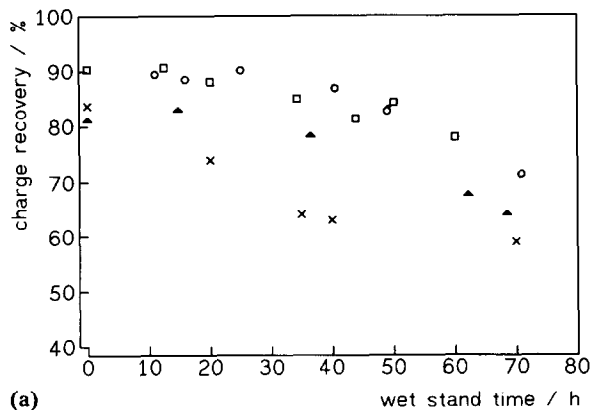
Various nitrogen-, oxygen-, sulfur- and fluorine-containing inorganic compounds were tested as additives to  $\text{LiClO}_4/\text{PC}$  electrolytes. The capacity losses of  $\text{LiC}_n$  electrodes and the cycling behaviour of metallic Li electrodes were used as easy-to-check criteria.

As a rule, fluorinated organic compounds did not show considerable beneficial effects. By contrast, some of the oxygen- and sulfur-containing compounds were highly effective. In particular, CO, CO-'reservoirs' like  $\text{Cr}(\text{CO})_6$ ,  $\text{N}_2\text{O}$  and polysulfides  $\text{S}_x^{2-}$  showed effects very similar to that of  $\text{CO}_2$ . We assume that, e.g., oxides, sulfides and nitrides of Li will be contained in films formed on Li in the presence of the above-mentioned additives. These multivalent anions may be much more suitable to build up thin and probably amorphous solid Li<sup>+</sup> electrolyte layers than monovalent anions such as fluoride or chloride.

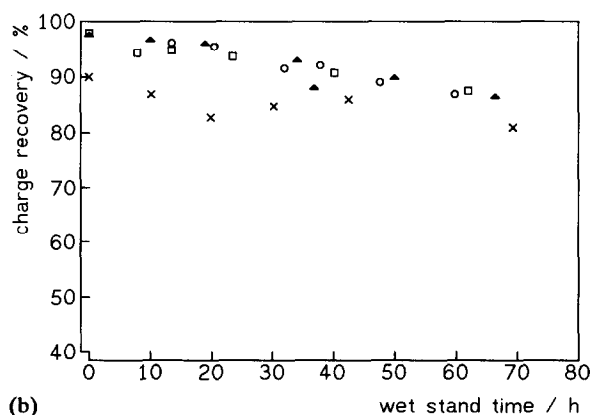
The effect of added  $\text{CO}_2$  in capacity losses of  $\text{LiC}_n$  anodes in  $\text{LiClO}_4/\text{PC}$  has been reported earlier [8]. Addition of  $\text{N}_2\text{O}$  or  $\text{S}_x^{2-}$  has very similar effects. First cycle capacity losses as well as second cycle capacity losses typically decrease by a factor of two (Fig. 1).

Summing up the capacity losses per cycle ( $L_n$ ) over a larger number of cycles ( $L_1 + L_2 + \dots + L_n$ ) shows that the additives strongly decrease the irreversible capacity losses in the first two cycles of  $\text{LiC}_n$  electrodes. After these two cycles even in the absence of additives a reasonable protective film has been formed and the beneficial effect of the additives is much less significant (Fig. 2). On the other hand, the improved self-discharge behaviour in the first few cycles may be quite important for 'ion batteries' which are assembled in the discharged state, i.e., with lithiated cathode materials.

Impedance studies of the films formed on carbon fibres during charge and discharge in  $\text{LiClO}_4/\text{PC}$  electrolytes containing  $\text{CO}_2$ ,  $\text{N}_2\text{O}$  or  $\text{S}_x^{2-}$ , respectively, clearly indicate



(a)



(b)

Fig. 1. Charge recoveries of P 100 fibres in 0.5 M  $\text{LiClO}_4/\text{PC}$  electrolytes during the (a) first charge/discharge cycle, and (b) second charge/discharge cycle; symbols: (x) no additive, (o)  $\text{CO}_2$  saturated, (square)  $\text{N}_2\text{O}$  saturated, (triangle)  $3 \times 10^{-4}$  M  $\text{S}_x^{2-}$ .

that these inorganic additives decrease the low frequency film resistances. This may be related with thinner polymer electrolyte layers.

The interpretation of impedance spectra was based on a simple equivalent circuit [10, 11] shown in Fig. 3 characterized by three semicircles, which are depressed because of a dispersion of time constants. The symbols  $R_{e1}$ ,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $C_1$ ,  $C_2$  and  $C_3$  denote the electrolyte resistance, the solid-state resistance of the film, the charge-transfer resistance, the diffusion resistance in pores of the film, a geometric capacity, the double layer capacity and an interfacial capacity, respectively. In this model, the low frequency semicircle is in fact a curved Warburg branch.

The impedance spectra shown in Fig. 4 were recorded in the first charge/discharge cycle of P-100-based  $\text{LiC}_n$  in  $\text{LiClO}_4/\text{PC}$ ,  $\text{LiClO}_4/\text{PC}-\text{CO}_2$ ,  $\text{LiClO}_4/\text{PC}-\text{N}_2\text{O}$  and  $\text{LiClO}_4/\text{PC}-\text{S}_x^{2-}$ , respectively. Current was reversed at  $n_{\min}$  (in  $\text{LiC}_n$ )  $\sim 7.5$ . The low frequency semicircles are continuously increasing, not only during charging but also during discharging.

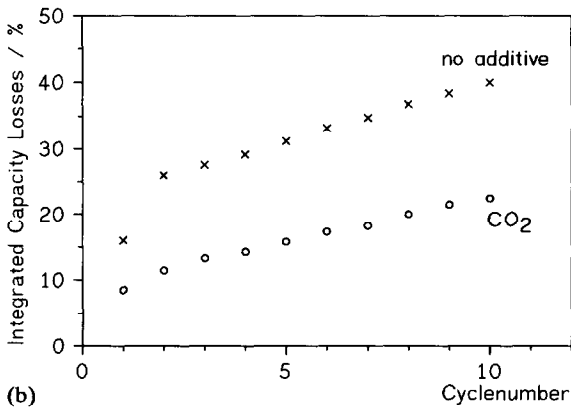
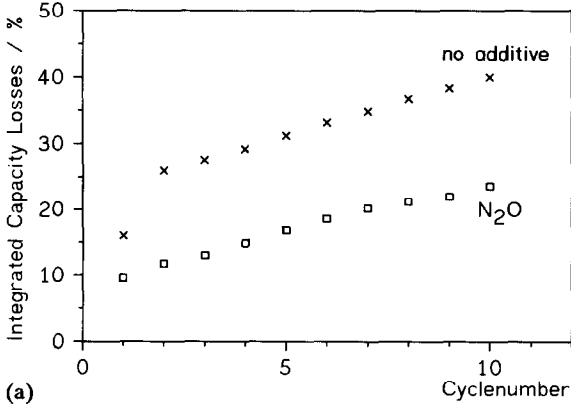


Fig. 2. Integrated capacity losses of LiC<sub>n</sub> electrodes in (a) N<sub>2</sub>O and (b) CO<sub>2</sub> containing electrolytes in comparison with LiClO<sub>4</sub>/PC.

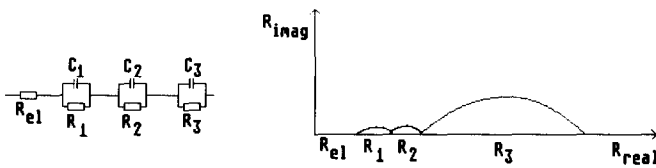
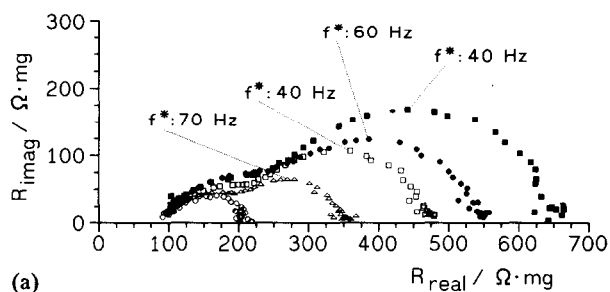


Fig. 3. Equivalent circuit for the observed impedance spectra of LiC<sub>n</sub>.

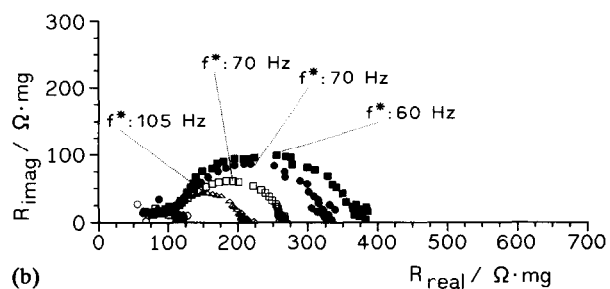
**Metallic lithium electrodes**

The effect of CO<sub>2</sub> and N<sub>2</sub>O on cycling of metallic Li may be illustrated by Fig. 5, comparing cycling ( $i_c = i_d = 1 \text{ mA/cm}^2$ ,  $Q = 2.7 \text{ C/cm}^2$ ) on a Ni substrate in an 'open' configuration without any separator. Under these conditions Li cannot be cycled in LiClO<sub>4</sub>/PC whereas addition of N<sub>2</sub>O (or CO<sub>2</sub>) improves very much the cycling behaviour. Similar but less drastic effects were observed with CO or CO-'reservoirs' (e.g. Cr(CO)<sub>6</sub>) as additives.

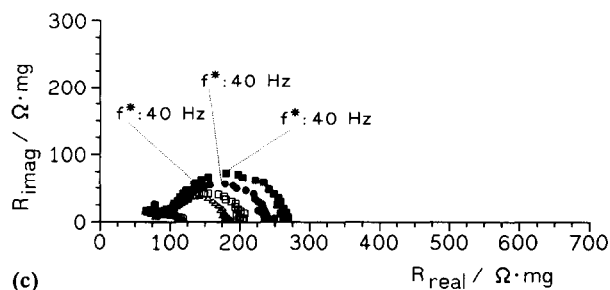
The effect of CO<sub>2</sub>, CO and N<sub>2</sub>O on the morphology of Li deposited from PC/LiClO<sub>4</sub> electrolytes was studied by scanning electron microscopy (SEM), Ni foil and



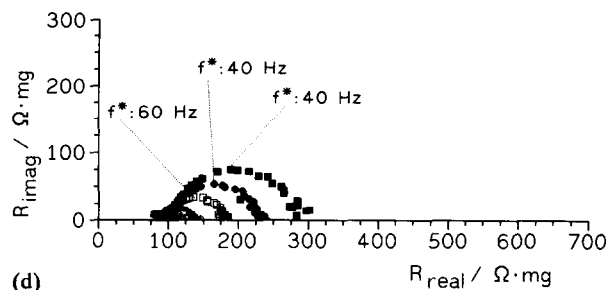
(a)



(b)



(c)



(d)

Fig. 4. Impedance spectra of P-100-based  $\text{LiC}_n$  electrodes during the first charge/discharge cycle in 0.5 M electrolytes. (a) PC/ $\text{LiClO}_4$ ; (b) PC/ $\text{LiClO}_4/\text{CO}_2$ ; (c) PC/ $\text{LiClO}_4/\text{N}_2\text{O}$  and (d) PC/ $\text{LiClO}_4/\text{S}_2^{2-}$ . Time required for charge/discharge cycle:  $\sim 450$  min, frequency range: 30 000–0.1 Hz. Symbols for  $n$  in  $\text{LiC}_n$ : charge (○)  $n \sim 100$ ; ( $\Delta$ )  $n \sim 11$ , and ( $\square$ )  $n \sim 8$ ; discharge: (●)  $n \sim 11$ , and ( $\blacksquare$ )  $n \sim 40$ .

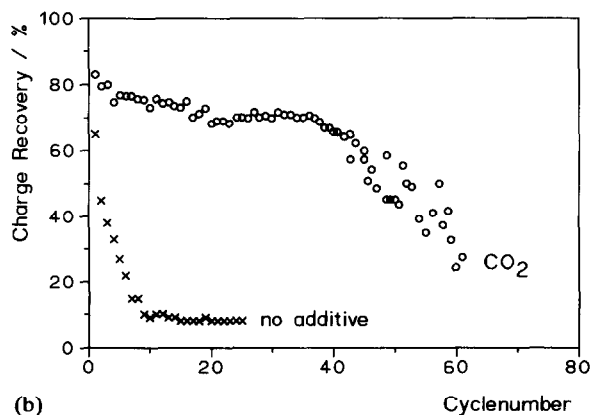
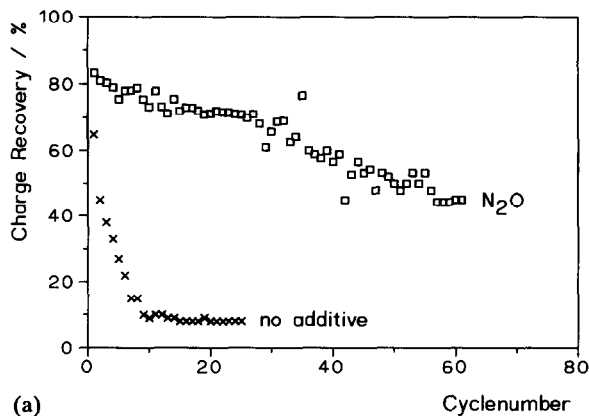


Fig. 5. Cycling of Li on Ni substrate in 'open' configuration (no separator, no force on deposited Li: (a) (x) 0.5 M LiClO<sub>4</sub>/PC, (□) 0.5 M LiClO<sub>4</sub>/PC-N<sub>2</sub>O; (b) (x) 0.5 M LiClO<sub>4</sub>/PC, and (○) LiClO<sub>4</sub>/PC-CO<sub>2</sub>.

Li foil being the substrates. A common feature of deposits obtained in the presence of these additives was their more compact and 'particle-like' [12] character, compared with the 'needle-like' Li obtained in pure LiClO<sub>4</sub>/PC (Fig. 6). In the presence of CO<sub>2</sub> and N<sub>2</sub>O much larger Li particles were observed. On the other hand, the larger particles seem to be 'embedded' in a material, which judging from its imaging behaviour in the electron microscope, is not a good electronic conductor.

## Conclusion

Various inorganic additives significantly improve the cycling behaviour of metallic Li as well as the self-discharge of C-Li electrodes. This beneficial effect is apparently related with the formation of protective films on the electrodes. In the case of the (almost) dimensionally-stable C-Li electrodes the formation of these films is mostly finished after a few cycles. Therefore, long-term stability and long-term availability of the additives in the electrolyte solution does not seem to be a crucial point. In the

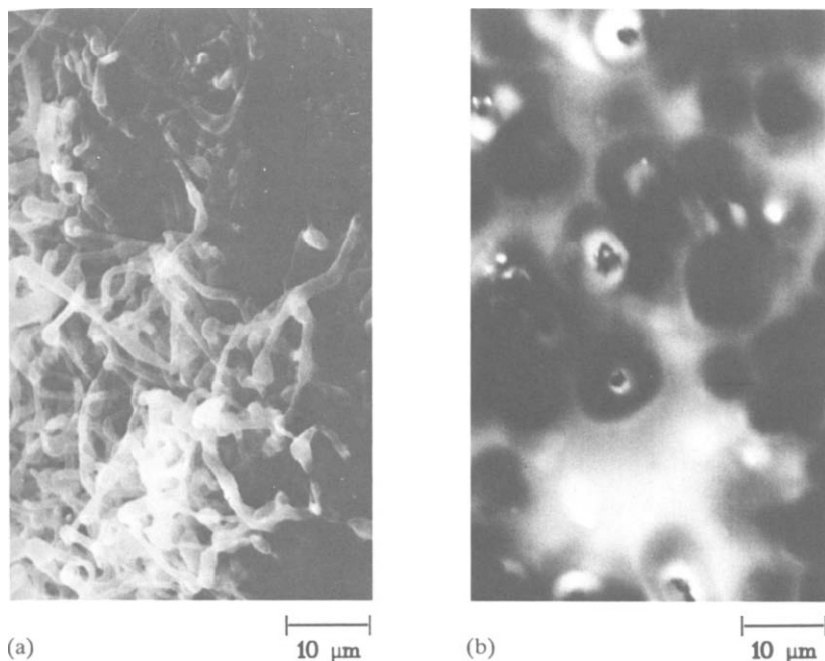


Fig. 6. SEM micrographs of Li deposited on Ni substrate: (a) 0.5 M PC/LiClO<sub>4</sub>, and (b) 0.5 M PC/LiClO<sub>4</sub> saturated with N<sub>2</sub>O;  $i = 1 \text{ mA/cm}^2$  and  $Q = 2.7 \text{ C/cm}^2$ .

case of metallic Li electrodes, however, the considerable electrochemical reactivity of all of these additives may be a serious drawback.

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### References

- 1 S.-I. Tobishima and T. Okada, *J. Appl. Electrochem.*, **15** (1985) 901.
- 2 J. O. Besenhard, J. Gürtler, P. Komenda and A. Paxinos, *J. Power Sources*, **20** (1987) 253.
- 3 J. O. Besenhard, P. Castella and J. Gürtler, *Bull. Electrochem.*, **6** (1990) 53.
- 4 V. R. Koch, *J. Power Sources*, **6** (1981) 357.
- 5 E. Plichta, S. Slane, M. Uchiyama, M. Salomon, D. Chua, W. B. Ebner and H. W. Lin, *J. Electrochem. Soc.*, **136** (1989) 1865.
- 6 S. B. Brummer, V. R. Koch and R. D. Rauh, in D. W. Murphy, J. Broadhead and B. C. H. Steele (eds.), *Materials for Advanced Batteries*, Plenum, New York, 1980, p. 123.
- 7 R. Fong, U. von Sacken and J. R. Dahn, *J. Electrochem. Soc.*, **137** (1990) 2009.
- 8 J. O. Besenhard, P. Castella and M. W. Wagner, in D. Tchoubar and J. Conrad (eds.), *Intercalation Compounds*, Trans. Tech. Publications, Zurich, 1992, p. 647.

- 9 P. A. Christensen, A. Hamnett, A. V. G. Muir and N. A. Freeman, *J. Electroanal. Chem.*, 288 (1990) 197.
- 10 J. G. Thévenin and R. H. Muller, *J. Electrochem. Soc.*, 134 (1987) 273.
- 11 J. G. Thévenin and R. H. Muller, *J. Electrochem. Soc.*, 134 (1987) 2650.
- 12 J.-I. Yamaki, *Proc. 5th Int. Meet. Lithium Batteries, Beijing, China, 1990*, p. 139.