

Improving the performance of graphite anodes in rechargeable lithium batteries

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Abstract

A low cost graphite was examined as a negative electrode for rechargeable lithium batteries. The use of an electrolyte solution consisting of LiPF_6 (1 mol dm^{-3}) in ethylene carbonate (EC) and dimethyl carbonate (DMC) at a volume ratio of 2:1 resulted in a capacity loss of 35% on the first cycle. When small quantities of dimethyl pyrocarbonate (DMPC) were added to the binary electrolyte system, the capacity loss on the first cycle was only 18% and thereafter a practical capacity value of 357 mA h g^{-1} was sustained for more than 50 cycles, representing more than 2000 h of cycling. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Graphite remains the material of choice for anodes in rechargeable lithium-ion batteries because of its high capacity, flat voltage and low cost. However, it is very sensitive to the electrolyte, which if not judiciously selected, may hinder reversible lithium intercalation into the graphite and cause unacceptable capacity loss on the first cycle. Other workers [1–3] have suggested that reversible lithium intercalation into graphite occurs only if the graphite surface is well protected by a suitable passivating film formed at potentials higher than the graphite intercalation potential.

Reducing the cost of materials used in lithium cells is an important driving force in industry, and we have therefore focussed on investigating the use of a low-cost graphite in association with an electrolyte solution based on 1 mol dm^{-3} LiPF_6 in a mixture of ethylene carbonate and dimethyl carbonate at a volume ratio of 2:1 and modified by the addition of a small known volume of pyrocarbonate. This electrolyte is electrochemically stable from 0–5 V [4].

2. Experimental

The graphite used was made available by Ultralife Batteries (UK). Battery grade ethylene carbonate and dimethyl carbonate (Grant Chemicals), and dimethyl pyrocarbonate (DMPC) from Aldrich, were used as received.

The solvent consisted of an EC:DMC mixture with a volume ratio of 2:1. While maintaining this ratio, ternary-component mixtures were prepared by adding known amounts of DMPC in the range of 5–20% of the total volume, V_t . To each of these mixtures, an appropriate quantity of LiPF_6 (Morita) was added to make an electrolyte solution of concentration of 1 mol dm^{-3} .

Composite electrodes were prepared by mixing graphite and polyvinylidene fluoride (PVDF) in a 95:5 wt.% ratio and grinding using mortar and pestle. The paste was dissolved in N-methylpyrrolidinone (NMP) using moderate heating under magnetic stirring for 15 h. The casting of the slurry was performed using a K-control coater KCC 302 (Erichsen). The copper substrate (Advent) was set on a grooved plate connected to a vacuum pump which maintained a flat surface. The slurry was cast by an adjustable micrometer scraper which controlled the thickness of the coating. The coatings were left to dry at room temperature for approximately 30 min, before vacuum drying at 110°C .

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for 15 h. The thickness of each composite electrode was in the range of 40 to 50 μm .

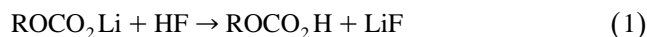
A three-electrode cell configuration was used for galvanostatic cycling, by means of a Macpile system (Biologic) with a lithium metal reference electrode, so that all potentials are quoted with respect to Li/Li^+ . Ac impedance measurements were taken at regular time intervals while polarising the cell without interruption, using a Solartron 1255 frequency response analyser and a Solartron 1286 potentiostat under computer control.

3. Results and discussion

Graphite was cycled in the standard unmodified electrolyte, LiPF_6 (1 mol dm^{-3})/2EC:1DMC at a current density of 0.14 mA cm^{-2} within voltage limits of 0.01–1.5 V. A plot of potential as a function of x in Li_xC_6 shows two plateaux at approximately +0.9 V and +0.5 V, followed by the usual staging plateaux encountered with graphite when intercalated with lithium. These features can be clearly seen in the incremental capacity plot ($\partial x/\partial E$ vs. E) in Fig. 1. Based on previous X-ray diffraction studies on lithiated graphite [5–7], the peaks at around 0.205, 0.104 and 0.084 V may be assigned to the two phase co-existence of the so-called ‘dilute stage 1’, also known as ‘stage 1’, and stage 4 (LiC_{36}), the ‘liquid-like stage 2’ (LiC_{18}) and ‘stage 2’ (LiC_{12}), and the ‘stage 2’ (LiC_{12}) and ‘stage 1’ (LiC_6), respectively. The peak at 0.9 V is

thought to be due to the formation of a passivating film [4] on the graphite surface. The cause of the extra peak at around +0.5 V is unknown. In an attempt to identify the process responsible, we modified the electrolyte slightly by changing the salt while maintaining the same solvent mixture. Solutions containing LiAsF_6 and LiBF_4 , each 1 mol dm^{-3} , were studied. The incremental capacity plots of the first cycle of each are shown in Fig. 2a and b, respectively. While the peak at around +0.5 V has vanished completely in the presence of LiAsF_6 , it remains unchanged with LiBF_4 . This suggests that this peak can be assigned to the reduction of species related to the anion of the salt. Note that the peak assigned to the formation of a passivating film appears at approximately +1.1 V in the LiAsF_6 -based electrolyte.

The coulombic efficiencies for the first cycle were 65%, 63% and 74% for electrolytes based on LiPF_6 , LiBF_4 and LiAsF_6 , respectively. The similarity of the results obtained in the LiBF_4 and LiPF_6 based-electrolytes is not surprising since it has been shown that even with the purest available form of these salts, HF is an unavoidable contaminant [8,9]. A substitution reaction between the products formed at +0.9 V and HF, similar to that occurring on metallic lithium may occur:



The resulting LiF-containing films formed at the surface are known to be poorly protecting [10] and as a result, anion reduction may occur at the graphite surface.

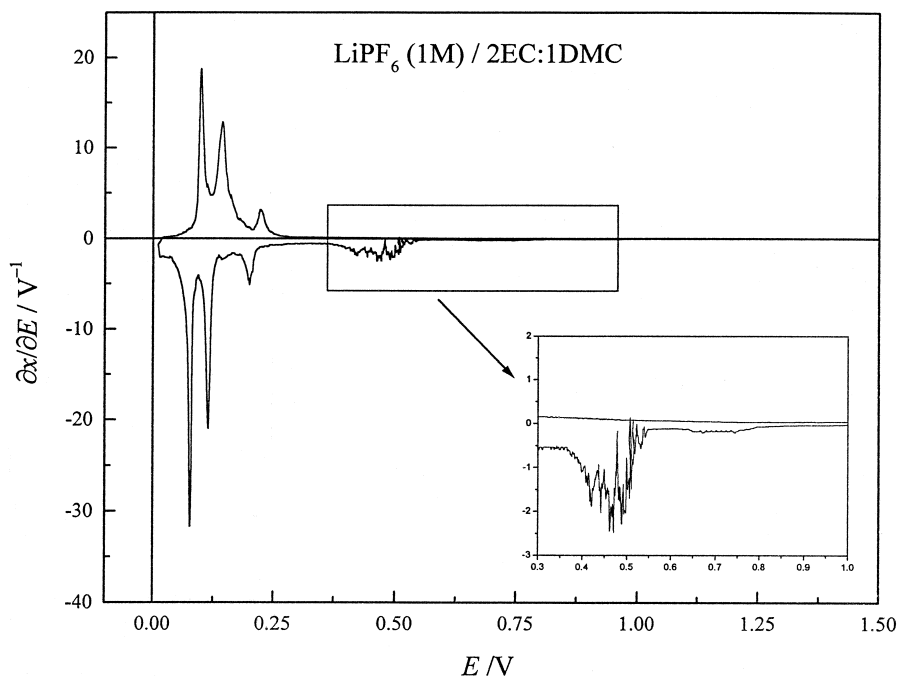


Fig. 1. Plot of incremental capacity of graphite cycled in LiPF_6 (1 mol dm^{-3})/2EC:1DMC solution at a current density of 0.14 mA cm^{-2} .

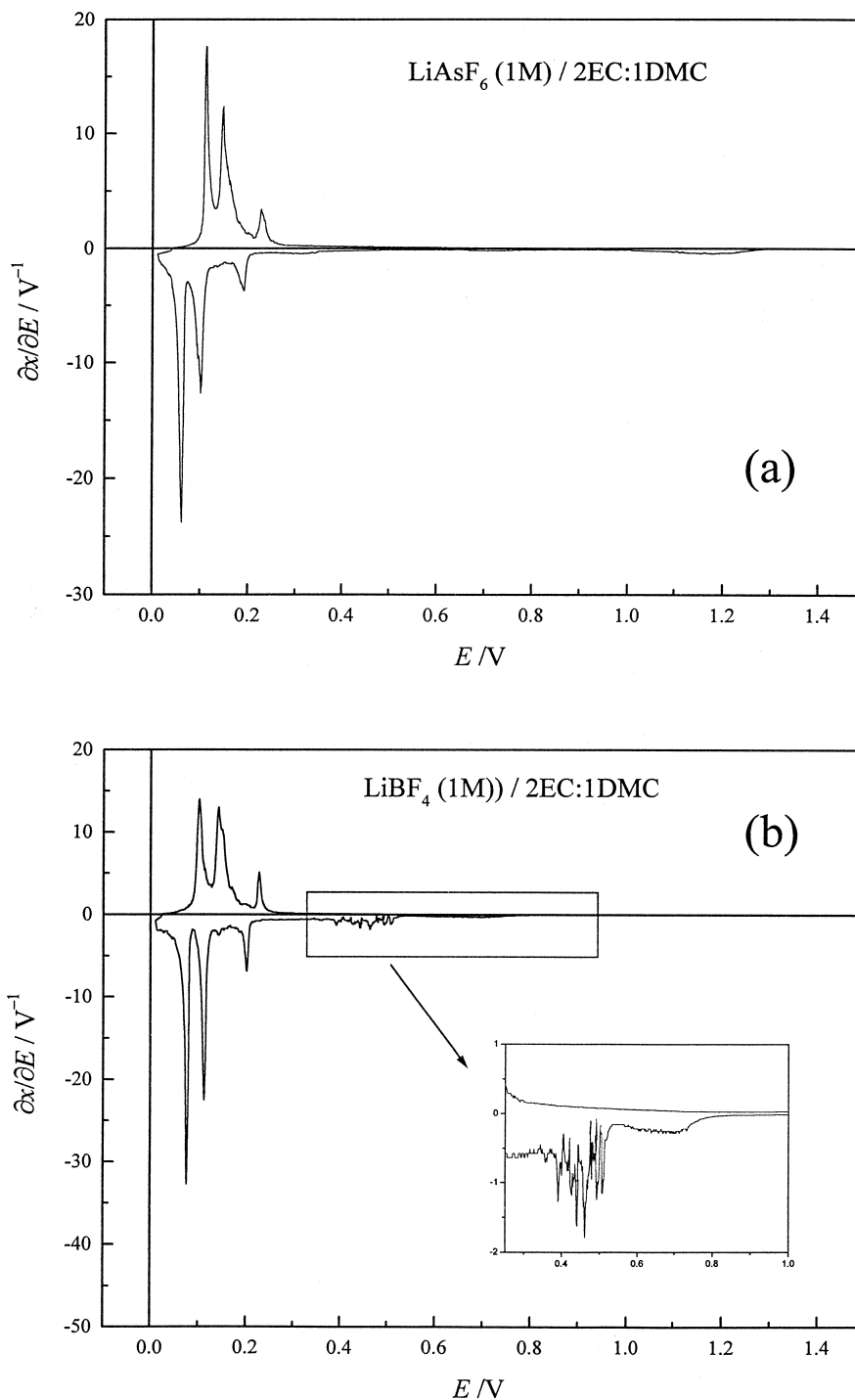


Fig. 2. Incremental capacity plot of graphite cycled at a current density of 0.14 mA cm^{-2} in 2EC:1DMC containing (a) LiAsF_6 and (b) LiBF_4 , each at 1 mol dm^{-3} .

A fully developed and compact passivating film consisting of lithium alkyl carbonates and lithium carbonate, isolating the graphite electrode from the electrolyte before it reaches the intercalation potential, is a prerequisite for efficient reversible lithium intercalation to occur into graphite [10,11]. In an attempt to decrease the capacity loss on the first cycle while retaining good cycle life and long

term high specific capacity, we carried out experiments in which graphite was cycled in an electrolyte solution based on a ternary solvent mixture of 2EC:1DMC with added DMPC. The choice of this additive was suggested by its decomposition products which are likely to yield carbon dioxide and hence lithium carbonate at a graphite anode. It is already known that the presence of CO_2 in an elec-

trolyte, leading to Li_2CO_3 , stabilizes the graphite surface [12].

3.1. Effect of DMPC as an Additive

Fig. 3a–c illustrate the incremental capacity $\partial x/\partial E$ vs. E plots for the first cycle of a graphite electrode cycled in a solution of LiPF_6 (1 mol dm^{-3})/2EC:1DMC with various additions of DMPC. In each case, the peak at $+0.5 \text{ V}$ was absent and this was associated with a significantly lower capacity loss (Table 1). The only source of capacity loss on the first cycle arises from the irreversible cathodic reduction responsible for the production of the efficient passivating film at 0.8 V – 1.0 V . The absence of the peak at $+0.5 \text{ V}$ suggests that the substitution reaction between the electrolyte reduction products formed at $+0.8 \text{ V}$ and HF from LiPF_6 is arrested. At high DMPC content the cathodic charge associated with this peak is increased.

To verify that CO_2 is indeed a beneficial agent with a similar effect at this graphite as the addition of DMPC, CO_2 gas, dried in a column of molecular sieves, was passed through the EC:DMC based electrolyte for about 3 h. Fig. 4 shows the incremental capacity plot of the first cycle for the graphite cycled in the CO_2 based electrolyte. The usual peaks related to the formation of a passivating film at around $+0.8 \text{ V}$ and the graphite intercalation compounds at potentials lower than $+0.2 \text{ V}$ are present. However, as in the case of the DMPC based electrolyte, the peak at $+0.5 \text{ V}$ was not present and the capacity loss on the first cycle was only 14%.

Table 1

Capacity loss measured after the first cycle for varying DMPC content

Solvent (volume ratio)	Capacity loss (%)
63EC:32DMC:5DMPC	18
60EC:30DMC:10DMPC	27
53EC:27DMC:20DMPC	27

Fig. 5 compares the variation of the specific capacity with cycle number of graphite cells cycled in the unmodified EC:DMC electrolyte with those containing DMPC or CO_2 , respectively. Both modified electrolytes combine low capacity loss on the first cycle with good capacity retention, although the specific capacity is slightly higher in the DMPC-based electrolyte. Indeed, a practical capacity of 357 mA h g^{-1} , close to the graphite theoretical capacity, is obtained after 50 cycles for the DMPC system.

3.2. Impedance studies

Fig. 6 illustrates the evolution of the impedance spectra with time of an electrolyte solution of LiPF_6 /2EC:1DMC at a graphite anode. A spike, characteristic of a blocking electrode was noted when the cell was held at the OCV, $+3.2 \text{ V}$. After polarising at $+0.65 \text{ V}$ for 15 min, a response consistent with two parallel RC components was evident. After 2 h, an increase in the total impedance was observed, the increase being more pronounced for the

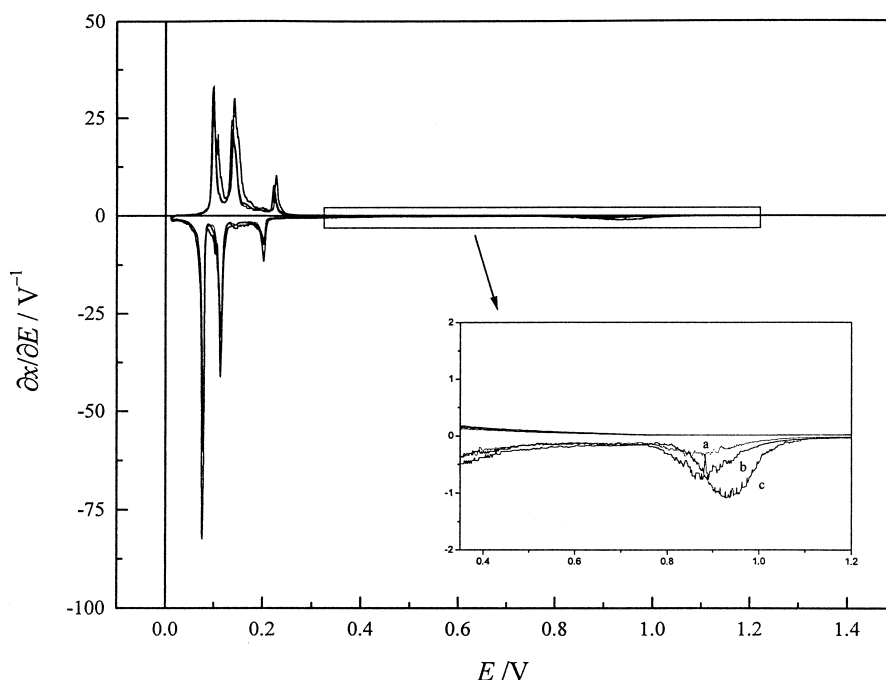


Fig. 3. Incremental capacity plot of graphite cycled in LiPF_6 (1 mol dm^{-3})/2EC:1DMC containing (a) 5% V_1 , (b) 10% V_1 and (c) 20% V_1 DMPC, each at a current density of 0.14 mA cm^{-2} .

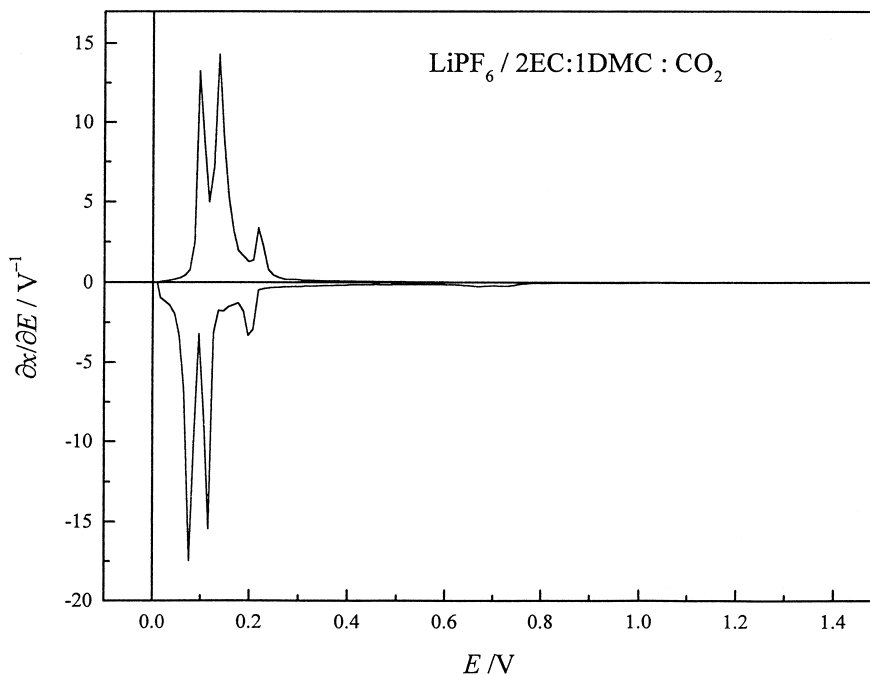


Fig. 4. Incremental capacity plot of graphite cycled in a LiPF_6 (1 mol dm^{-3})/2EC:1DMC solution saturated with CO_2 at a current density of 0.14 mA cm^{-2} .

semi-circle in the low frequency range. The cell was further polarised at $+0.35 \text{ V}$ and the evolution of impedance spectra with time (Fig. 6b) showed a steady increase in the total impedance over a 17 h period.

Similar measurements were conducted on a graphite electrode polarized at $+0.6 \text{ V}$ using the DMPC-modified electrolyte. Again, an increase in the total impedance with

time was observed (Fig. 7). The impedance value, however, stabilised more rapidly and was slightly lower than the previous case. A further polarization step at $+0.3 \text{ V}$ (Fig. 7b) showed that, after an initial decrease, the total impedance after 17 h was only slightly greater than that observed after completion of the first potential step to $+0.6 \text{ V}$.

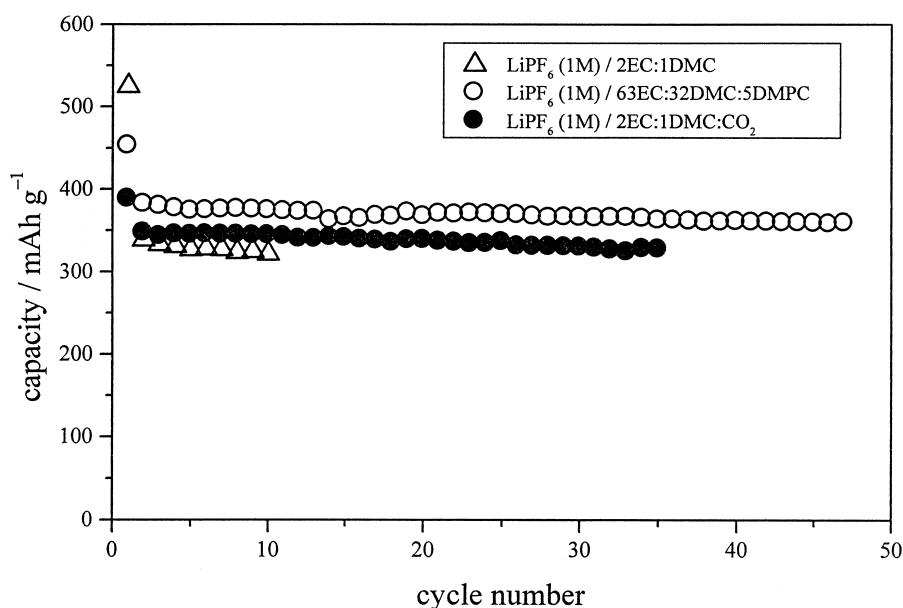


Fig. 5. Specific capacity vs. cycle number of graphite cycled in 2EC:1DMC, 2EC:1DMC:5% V_1 DMPC and 2EC:1DMC: CO_2 , each containing LiPF_6 (1 mol dm^{-3}), at a current density of 0.14 mA cm^{-2} .

Fig. 8 compares the impedance spectra after 17 h polarisation at about +0.3 V of two graphite cells containing the EC:DMC based electrolyte solutions with and without additional DMPC. The total impedance of the system containing DMPC is much smaller than with the standard binary 2EC:1DMC solution. These findings are consistent with the galvanostatic data obtained on the first cycle. The reduction of a LiPF_6 electrolyte solution in 2EC:1DMC at a graphite surface may give rise to reduction products precipitating out as a film containing LiF. Such processes, in particular those occurring at about

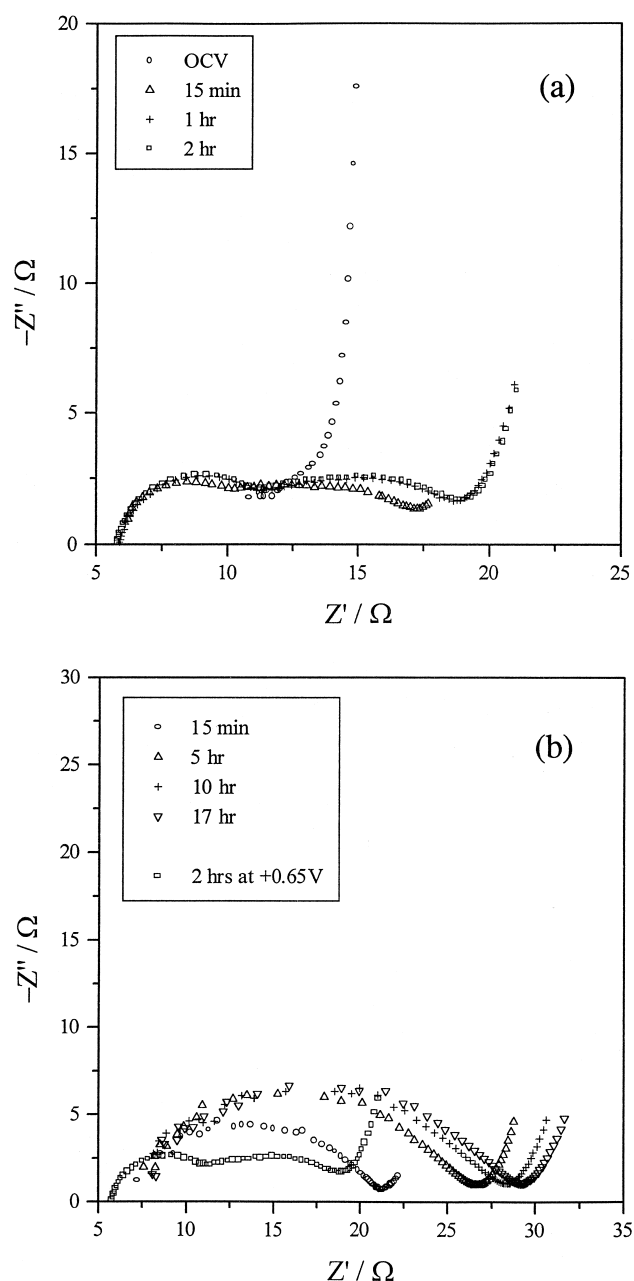


Fig. 6. Impedance spectra of a low-cost graphite cell in LiPF_6 (1 mol dm^{-3})/2EC:1DMC polarised at (a) +0.65 V and (b) +0.35 V.

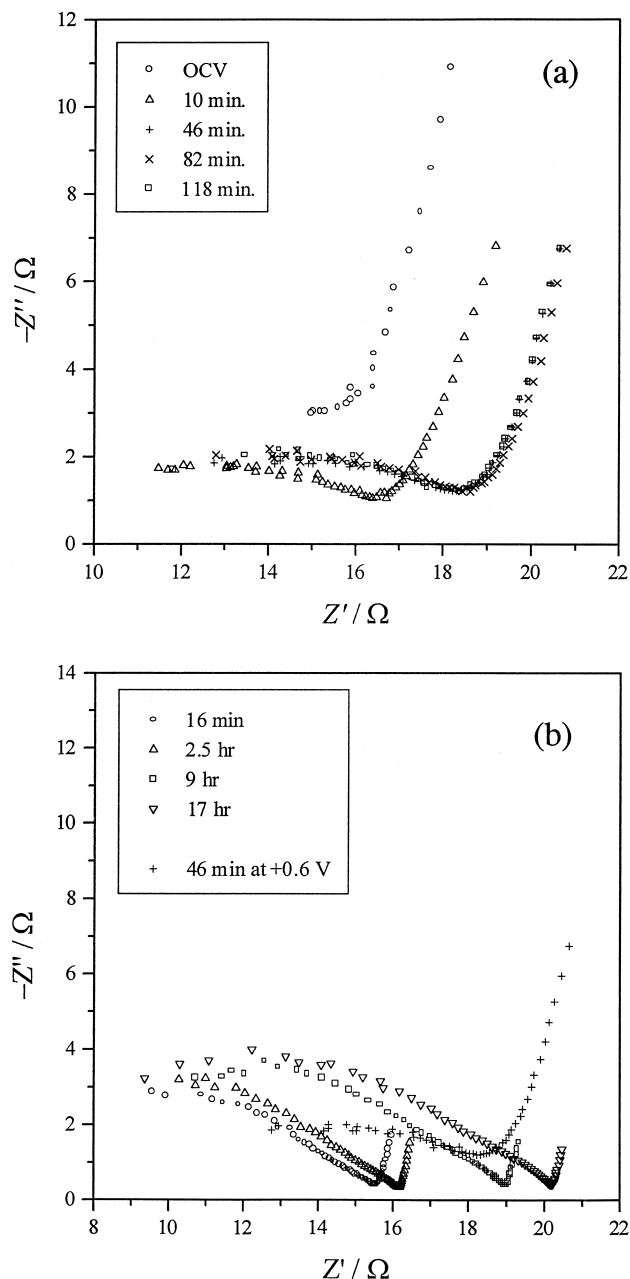


Fig. 7. Impedance spectra of a graphite cell in LiPF_6 (1 mol dm^{-3})/63EC:32DMC:5DMPC polarised at (a) +0.6 V and (b) +0.3 V.

+0.5 V, are suppressed on addition of small quantities of DMPC.

4. Conclusions

A graphite electrode was investigated as an anode for rechargeable lithium batteries. Using an electrolyte consisting of 1 mol dm^{-3} LiPF_6 in 2EC:1DMC, a capacity loss of 35% was found on the first cycle. Addition of up to 5% by volume of DMPC to the solution suppressed the irreversible reaction at +0.5 V resulting in a capacity loss of only 18% on the first cycle. A practical capacity of 357

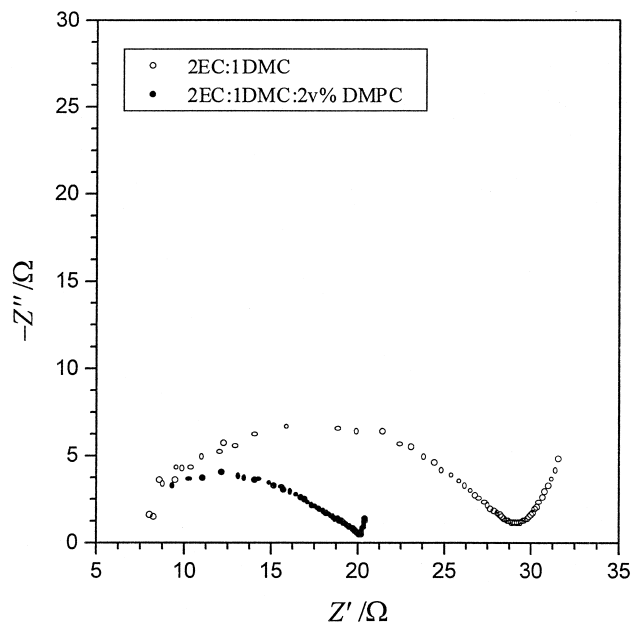


Fig. 8. Impedance spectra of graphite cells in (a) 2EC:1DMC and (b) 63EC:32DMC:5DMPC, each containing LiPF_6 (1 mol dm^{-3}).

mA h g^{-1} was obtained after 50 cycles which represents more than 2000 h of cycling.

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