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The use of S,S-dialkyl dithiocarbonates in Li ion battery electrolytes

Abstract S,S-dialkyl dithiocarbonates such as S,S-dimethyl dithiocarbonate and S,S-diethyl dithiocarbonate were tested as solvents for rechargeable lithium ion batteries. Graphite electrodes can be successfully cycled at high reversible capacities in an S,S-dimethyl dithiocarbonate solution containing 1 M $LiAsF_6$, while lithium ions cannot intercalate into graphite in S,S-diethyl dithiocarbonate solutions. Fourier transform infrared spectroscopy, cyclic voltammetry and chronopotentiometric methods were used in order to monitor the reaction mechanism.

Key words S,S-dialkyl dithiocarbonates · Graphite · Intercalation · Li ion battery

Introduction

The electrolyte solution to be used in lithium ion batteries is a key factor which can influence the performance of the cell. The quality of the surface film developed on the carbon electrode at low potentials is important in order to maintain high cycle life on the anode [1–3]. Most solvents and salts are reduced on the carbon anode and form passive layers which are lithium ion conductors known as solid-electrolyte interfaces (SEI) [4].

Recent work in our laboratory [5, 6] has demonstrated the feasibility of using sulfur dioxide (SO_2) as a passivating agent for the graphite anode. We have found that SO_2 can serve as an excellent surface modification agent to produce a fully developed passive film. These passive layers, composed of Li_2S and Li-oxysulfur compounds are primarily responsible for the improved characteristics of the graphite anode upon repeated cycling. The next step in our research was to use alkyl carbonate solvents which already contain sulfur atoms in their molecular structures. Two dithiocarbonates, diethyl and dimethyl dithiocarbonates (DETC and DMTC), which are analogs of diethyl and dimethyl carbonate (DEC and DMC), were tested for the first time as a solvent electrolyte containing 1 M $LiAsF_6$ in a lithium-graphite cell.

Here we report on the influence of the sulfur compounds used on the electrochemical performance of the graphite anode. Cyclic voltammetry and Fourier transform infrared (FTIR) spectroscopy along with chronopotentiometric methods were employed in order to understand the nature of the passivation films formed on the graphite electrodes cycled in these solvents.

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Experimental

Carbon electrodes were prepared from Timrex SFG44 synthetic graphite powder (4.5 m^2/g, Timcal America) by slurrying the carbon material with a 10-wt% solution of PVDF (polyvinylidene fluoride, Atochem, North America), dissolved in NMP (N-methyl-2-pyrrolidinone, Aldrich). The mixture was rolled onto copper foil (0.025-mm thick), dried, pressed and sintered at 120 °C under vacuum for several hours. The theoretical capacities of the graphite electrodes were around 2 mAh, based on a fully charged stoichiometry of LiC_6. The graphite electrode performance was measured against Li metal foil (Cyprus Foote Mineral, 0.25-mm thick) as a counter electrode (separated from the graphite with Whatman BS-65 glass microfibers) in a two-electrode Tee-cell configuration [7]. The graphite electrodes were cycled galvanostatically (intercalation-deintercalation) between 1.5 and 0.001 V using a MACCOR series 4000 battery cycler.

The solvents used in this study were dimethyl and diethyl carbonate (DMC and DEC, Grant Chemicals) and S,S-dimethyl and diethyl dithiocarbonate (DMTC and DETC, TCI America). $LiAsF_6$ (Lithco) was used as received with a final concentration of 1 mole/liter. The water content of the prepared electrolyte was determined with the use of a Model DL18 Mettler Karl Fischer apparatus and was typically less than 30 ppm.

Conductivity values of the various electrolytes were determined by using a conductivity cell (YSI, Ohio, Model 3403) with a cell constant of 1. Cyclic voltammetry studies on the electrolytes were performed using an EG&G Princeton Applied Research potentiostat/galvanostat Model 263A under the control of EG&G 270 software. All measurements were made at a Pt disk electrode (0.2 cm^2, sealed in glass) in a three-electrode glass cell with the use of Li counter and reference electrodes. All potentials are quoted with respect to the Li/Li$^+$ couple. The surface chemistry of the graphite electrodes was studied ex situ by pelletizing the graphite particles with KBr and using Fourier transform infrared spectroscopy (FTIR, Nicolet 400D) in transmittance mode. The FTIR spectrum obtained from a KBr pellet (Aldrich, FTIR grade) or window (Wilmad, N.J.) served as a background spectrum in all the transmittance measurements.

Results and discussion

Table 1 presents the specific conductance values (mS cm^{-1}) for solutions of dimethyl and diethyl carbonate (DMC and DEC) and for S,S-dimethyl and S,S-diethyl dithiocarbonate containing 1 M LiAsF$_6$. The change of the oxygen atoms to sulfur reduces the conductivity values. As expected, Table 1 shows that when an oxygen atom is replaced by sulfur in alkyl carbonate solvent, the viscosity and density of the solvents are influenced. Hence, the conductivity values obtained from the thiocarbonates are lower by some orders of magnitude than the values obtained from the organic alkylcarbonates. It is worth noting that LiAsF$_6$ could not be dissolved into DETC at a concentration of 1 mole/liter and that a solution of only 0.5 mole/liter could be obtained.

The voltammetric behavior of DMTC

Lithium is not stable at all in DETC, since no stable passive layers are created at the lithium-electrolyte interface. This behavior resembles that of lithium metal in the analogous solvent DEC [9], in which the process of the lithium corrosion does not stop at any time. Therefore, graphite electrodes could not be cycled in DETC single-solvent electrolytes. Figure 1a shows a typical first-cycle voltammogram [scan rate of 20 mV/s, starting from open circuit voltage (OCV) and proceed-

ing in the cathodic direction] obtained at a Pt working electrode in solutions of DMC and DMTC containing 1 M LiAsF$_6$. By analyzing the voltammograms obtained from the two different electrolytes, one can observe that for both electrolytes the reduction peak positions are almost the same. Since the specific conductance value of the DMC solution is higher than that of the DMTC solution, one can expect higher currents to be observed during the DMC cathodic scan. However, the peaks at around 1.5 V and below 0.8 V are attributed to electrolyte reduction processes. The anodic peaks at 0.6 and 1.2 V are due to oxidation of surface oxides on the Pt working electrode. These films are created instantly after the cleaning and polishing of the Pt electrode. The disappearance of these peaks after the completion of the cathodic scan can indicate whether the electrode is fully passivated.

Figure 1b presents cyclic voltammograms (20 mV/s) obtained by consecutive sweeps at Pt electrodes in DMC and DMTC containing 1 M LiAsF$_6$. The two sets of voltammograms are different from each other. While the Pt is passivated after the first cathodic sweep in the DMC electrolyte, the reduction products of DMTC do not fully passivate the Pt electrode because of participation by the reduction products to form the SEI [4]. The cathodic current peaks at 1.5 V and below 1 V, which are related to electrolyte reduction processes, continue to appear upon cycling, while the anodic peaks related to oxidation of the initial Pt films continue to appear as well. All this evidence leads to the conclusion that DMC passivates the Pt working electrode much more efficiently than DMTC.

One of the features required in an electrolyte is high voltage stability. For that purpose we studied the stability of DMTC toward oxidation and we compared it to DMC. In Fig. 1c, we show the cyclic voltammograms (20 mV/s, starting from OCV and proceeding in the anodic direction) obtained at Pt in solutions of DMC and DMTC containing 1 M LiAsF$_6$. While the DMC solution is stable toward oxidation (current density ≤ 50 μA/cm^2) up to 4.7 V, the DMTC solution is stable only up to 4 V. This difference in the oxidation potentials is not a surprise. The DMC molecule contains two oxygen atoms which possess strong electron affinity. In DMTC, the oxygens are replaced by sulfur atoms which have a weaker electron affinity, and as expected the oxidation potential is changed as well.

The correlation between the electrochemical behavior of graphite-lithium electrodes and the surface films formed in DMC and DMTC

Figure 2a presents the voltage (V)-capacity (mAh) profiles of graphite electrodes cycled against a lithium counter electrode in a DMTC solution containing 1 M LiAsF$_6$. We observed the existence of a large irreversible capacity in the first intercalation cycle. This irreversible capacity is consumed in the voltage range

Table 1 Physical properties of dimethyl and diethyl carbonate and S,S-dimethyl and diethyl dithiocarbonate

Solvent	Density (g/cm^3)	Viscosity η (cP)	Specific conductance 1 M LiAsF$_6$ (mS cm^{-1})
DMC[a]	1.069	0.58	8.6
DMTC[b]	1.19	0.78	1.7
DEC[a]	0.975	0.75	4.1
DETC[b]	1.09	0.97	0.04[c]

[a] Data taken from [8]
[b] Data provided by manufacturer
[c] Data obtained from a solution of 0.5 M LiAsF$_6$ at 20 °C

1.5–0.3 V, in order to produce the lithium ion conductive passive layers. While DMC is clearly incompatible with the graphite negative electrode [1–3, 5], we discovered that, when DMTC is used as a solvent, a graphite electrode can fully intercalate and deintercalate
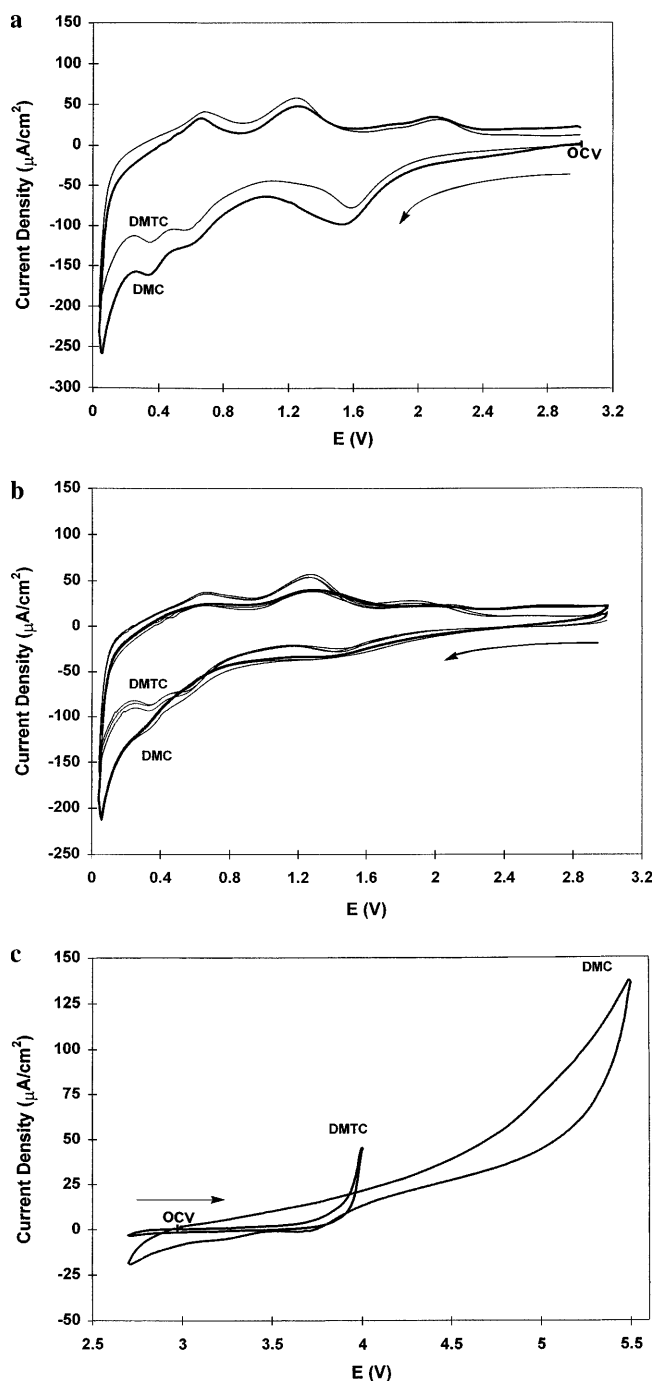
lithium ions. However, the passive films are not stable, although high-capacity reversible lithium ion intercalation-deintercalation processes are observed. This phenomenon is demonstrated by the gap between the discharge (intercalation) and the charge capacities (deintercalation) as shown in Fig. 2b.

We conclude from this behavior that DMTC reduction products create a passive film which enables lithium ions to migrate efficiently into the graphite lattice, but these films are also unstable and tend to dissolve into the solution, causing the passive layer to be formed again upon repeated cycling.

Figure 3 presents FTIR spectra obtained from DMC, DMTC, and from a graphite electrode cycled against a lithium counter electrode in DMTC/ 1 M LiAsF$_6$. The FTIR spectra were obtained ex situ by using KBr windows (for the neat solvents) or by pelletizing the graphite powder (after washing with 2Me-THF) with KBr powder. All spectra were measured in the transmittance mode. The FTIR spectrum
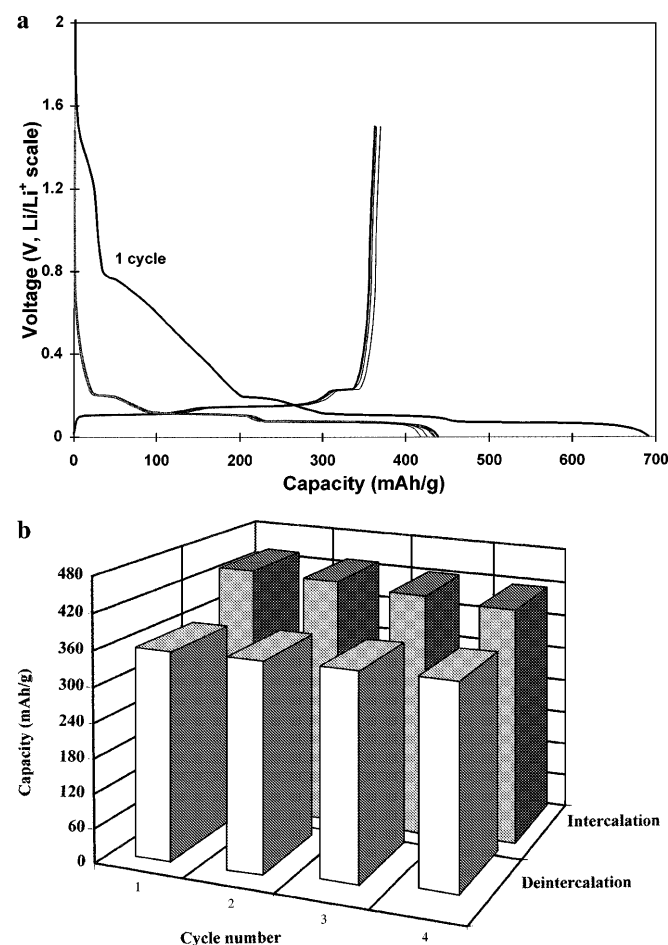

Fig. 1a–c Cyclic voltammograms (scan rate 20 mV/s) obtained at a Pt working electrode in solutions of DMC and DMTC containing 1 M LiAsF$_6$. Li metal served as a counter and a reference electrode. **a** Cathodic sweeps (starting from OCV and proceeding in the cathodic direction). **b** Consecutive cathodic sweeps. **c** Anodic sweeps (starting from OCV and proceeding in the anodic direction)

Fig. 2 a The voltage (V) – capacity (mAh/g) profiles and **b** the capacity gap (expressed in mAh/g) between the discharge (intercalation process) and the charge (deintercalation process) capacities of graphite electrodes cycled against lithium metal counter electrodes in DMTC solutions containing 1 M LiAsF$_6$ at a current density of 0.1 mA/cm^2 ($\sim$C/20). Data shown for the first 5 cycles
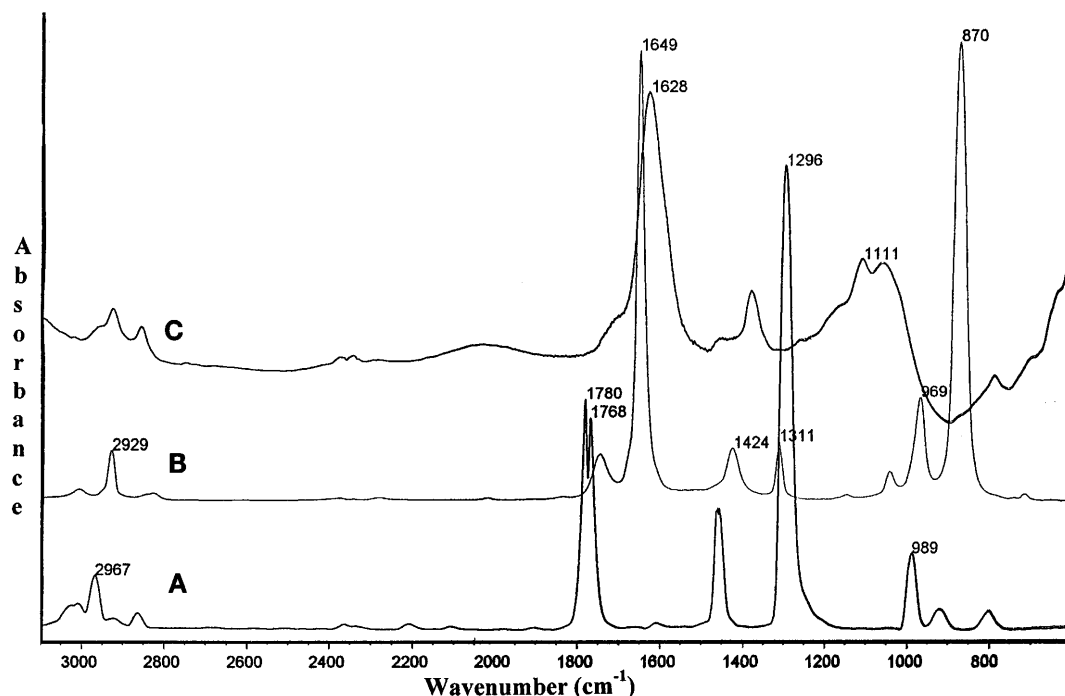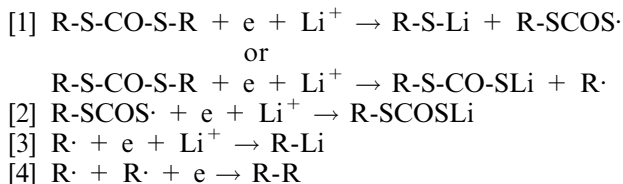
230

Fig. 3 FTIR spectra (ex situ, transmittance mode) obtained from **a** DMC, **b** DMTC, and **c** a graphite electrode which was previously cycled against a lithium metal counter electrode in DMTC/1 M LiAsF$_6$

obtained from a graphite electrode cycled in DMC solutions has been described in [10]. Spectrum c, obtained from a graphite electrode cycled in DMTC solution, has the pronounced lithium alkyl dithiocarbonate (Li-SCOSCH$_3$) IR peaks [1630 cm^{-1} ($\nu_{C=O}$, asymmetric) and 1379 cm^{-1} ($\nu_{C=O}$, symmetric)], which appear at a lower wavenumber than the expected peaks for lithium methyl carbonate (the main reduction product of DMC), which appear at 1650 and 1390 cm^{-1} [10].

The IR peaks at 2950–2850 cm^{-1} are related to ν_{C-H} of the methyl group in LiSCOSCH$_3$, while the 1060–1110 cm^{-1} (ν_{C-S}) and 800 cm^{-1} (δ_{SCOS}) peaks are attributed to the lithium methyl dithiocarbonate. We do not have any evidence for the formation of Li$_2$COS$_2$ (the analogue of Li$_2$CO$_3$), since one would expect these IR peaks to appear at 1400–1550 cm^{-1} and at ~860 cm^{-1}.

Based on the IR, we can outline a path for the reduction of the S,S-dialkyl dithiocarbonate in the presence of Li-ions.

[1] R-S-CO-S-R + e + Li$^+$ → R-S-Li + R-SCOS·
    or
    R-S-CO-S-R + e + Li$^+$ → R-S-CO-SLi + R·
[2] R-SCOS· + e + Li$^+$ → R-SCOSLi
[3] R· + e + Li$^+$ → R-Li
[4] R· + R· + e → R-R

It is likely that the presence of sulfur atoms in the passive layer, as shown in our earlier work [5, 6], enables lithium ions to intercalate into the graphite, whereas this process does not occur to completion when sulfur-free DMC is used.

Conclusions

We have explored for the first time the possibility of using a new solvent family, S,S-dialkyl dithiocarbonates. Our study shows that although this solvent family has large disadvantages such as very low conductivity values of the lithium salt solutions, low ion dissociation, low oxidation potentials (< 4 V) and high cost, the sulfur atoms in DMTC allow the formation of an SEI which enables the lithium ions to intercalate-deintercalate into the graphite lattice.

These passive films, although partially unstable, as evidenced by cyclic voltammetry and graphite cycling data, permit Li ion migration without any interaction with the solvent molecules, which usually leads to graphite lattice destruction. We conclude that it will be worthwhile to look into other solvents containing sulfur or even phosphorus and nitrogen atoms in their structures as well.

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