Short communication

Effect of solvents and solvent mixtures on intercalation/de-intercalation behaviour of Li^+ and ClO_4^- ions in polypropylene–graphite composite electrodes

V. Suryanarayanan[a,*,1], M. Noel[b]

[a]*Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan*
[b]*Central Electrochemical Research Institute, Karaikudi 630006, India*

Abstract

The intercalation of Li^+ and ClO_4^- ions in polypropylene–graphite composite electrodes in different single solvents and 1:1 binary solvent mixtures is studied by means of cyclic voltammetry and scanning electron microscopy. The intercalation/de-intercalation efficiency as a potential dual-intercalation battery electrode for cationic intercalation (positive electrode) is found to be generally lower than that for anionic intercalation in most of the solvents. 1:1 solvent mixtures do not enhance intercalation/de-intercalation efficiency significantly beyond the values found in a single solvent. The mixed-solvent system leads, however, to less co-solvent intercalation and graphite exfoliation, and hence better cycle-life as a potential battery electrode. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Solvent mixtures; Graphite lattice; Dual intercalation; Graphite exfoliation

1. Introduction

Considerable attention is being focused on graphite intercalation compounds [1], with special reference to the performance of graphite negative electrodes for lithium-ion batteries [2]. Apart from the nature and type of graphite substrate, the choice of supporting electrolyte as well as solvent significantly influences the electrode efficiency [3]. In addition to conventional non-aqueous solvents like acetonitrile (AN), dimethyl formamide (DMF), dimethylsulfoxide (DMSO) and methylene chloride, a number of new solvents such as ethylene carbonate (EC), diethyl carbonate (DEC) [4,5], methyl propyl carbonate [6] and trifluoro propylene carbonate [7] as well as their mixtures have been used [8]. Poly(vinylchloride) as well as related poly electrolytes [9,10] and other organic electrolytes [11] have also been investigated. Among the new supporting electrolytes are lithium trifluoro methane sulfonate and lithium hexafluoro phosphate [12]. Co-insertion of solvents with ionic species is one of the main causes of capacity loss and lower

cycle-life in intercalation-based battery systems [13,14]. Addition of ethylene sulfite [15] and propylene sulfite [16], along with propylene carbonate, is found to decrease the exfoliation of graphite lattices.

Development of a new type of battery system involving dual-intercalation of anionic and cationic species on two graphite electrodes as negative and positive plates is attracting present interest. The first search for a dual-intercalation system was reported in molten electrolyte [17]. Subsequently, the possibility of a dual-intercalation battery system based on intercalation of ionic species such as tetralbutyl ammonium perchlorate [18] and lithium perchlorate [19] from propylene carbonate medium on graphite electrodes has been reported from this laboratory. The effect of conventional solvents like AN, DMF and DMSO on cationic as well as anionic intercalation was also studied [20].

Though there are many reports dealing with anionic as well as cationic intercalation/de-intercalation processes, from different non-aqueous solvents, there is no direct comparison of all these different solvents/solvent mixtures under identical experimental conditions. Further, the effect of formation of solid-electrolyte interface (SEI) films on Li^+ and ClO_4^- ions transport on graphite material in different solvents and the stability of host material against solvent co-intercalation has not been studied in detail. A polypropylene–graphite composite (CPP) electrode which exhibited

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* Corresponding author. Fax: +886-2-23623040.
E-mail address: sur_2000_99@yahoo.com (V. Suryanarayanan).
[1] Presently Post-Doctoral Fellow at the Department of Chemical Engineering, National Taiwan University, Taipai, Taiwan.

better stability as well as reproducibility in non-aqueous solvents [18,21] has been chosen in this work.

2. Experimental

A rod (3 mm diameter) of the CPP sample was fitted tightly into Teflon and used as the working electrode. The electrode was polished to a minor finish using emery papers (1/0 to 5/0) and the reversibility was checked with a ferri-cyanide/ferrocyanide redox system. A saturated calomel reference electrode and a platinuim counter electrode were used. Analar grade non-aqueous solvents such as PC, EC, DEC, dimethoxy ethane (DME) and sulfolane and possible combinations of these binary mixtures (1:1) were employed. Analar grade $LiClO_4$ was dried in vacuum dessicator.

Cyclic voltammetry was performed with a potentiostat (Wenking Laboratory model LB75L), a voltage scan generator (Wenking model VS672), and an X-Y recorder (Rikadenki model RW-201T. A JEOL model (model 30CF) scanning electron microscope (SEM) was used to examine the intercalated electrodes. The experiments were performed at 273 ± 1 K.

3. Results and discussion

Typical multisweep cyclic voltammograms (sweep rate = 40 mV s^{-1}) obtained for cathodic Li$^+$ ion and anodic ClO_4^- ion intercalation/de-intercalation processes in PC medium with 0.25 M $LiClO_4$ are shown in Fig. 1(a) and (b), respectively. The intercalation/de-intercalation process is found to be quite reversible and can be repeated a number of times under identical experimental conditions [18]. The retraceability of multi-sweep voltammetric curves during

anion intercalation is close to 100% (Fig. 1(b)), while for cation intercalation, the cathodic charge decreases slightly with sweep number (Fig. 1(a)). The intercalation charge (Q_{in}), de-intercalation charge (Q_{de}), intercalation/de-inter-calation efficiency (IDE = Q_{de}/Q_{in}), threshold potential (E_{th}) and de-intercalation peak potential (DPP) obtained at a sweep rate of 40 mV s^{-1} are presented in Tables 1 and 2. For Li$^+$ ions, the IDE is 33%, and for ClO_4^- ions is 70%. The reversibility of the cyclic voltammogram suggests that the intercalation reaction proceeds smoothly through the solid-electrolyte interface (SEI) without further decomposition of solvent. The IDE value increases with increase in concentration of supporting electrolyte (Tables 1 and 2).

Typical cyclic voltammograms for the dual intercalation/de-intercalation behaviour of Li$^+$ and ClO_4^- ions in PC/DME are shown in Fig. 2(a) and (b). Once again, the process is quite reversible and can be recycled. For Li$^+$ ions, the IDE is 30% (Table 2) and for ClO_4^- ions is 33%.

The cyclic voltammetric data for perchlorate anion intercalation in different solvents/binary solvent mixtures with IDEs above 40% are presented in Table 1. AN and sulfolane show an IDE of 59 and 48%, respectively. The addition of EC to sulfolane markedly increases the efficiency whereas the addition of PC and DEC have only little effect. Further, the addition of DEC to PC lowers the efficiency of PC. The results show that in case of single solvents, PC shows a maximum IDE of 70%; EC/sulfolane is found to be an efficient binary solvent mixture for perchlorate ion (IDE = 66%).

Similarly, the cyclic voltammetry data for Li$^+$ ion in different solvents/binary solvent mixtures are presented in Table 2. DME shows the same IDE value as PC, while sulfolane has a still lower value. The addition of DME to PC has only little effect and addition to EC does not significantly improve the efficiency. Further, the intercalation/de-inter-
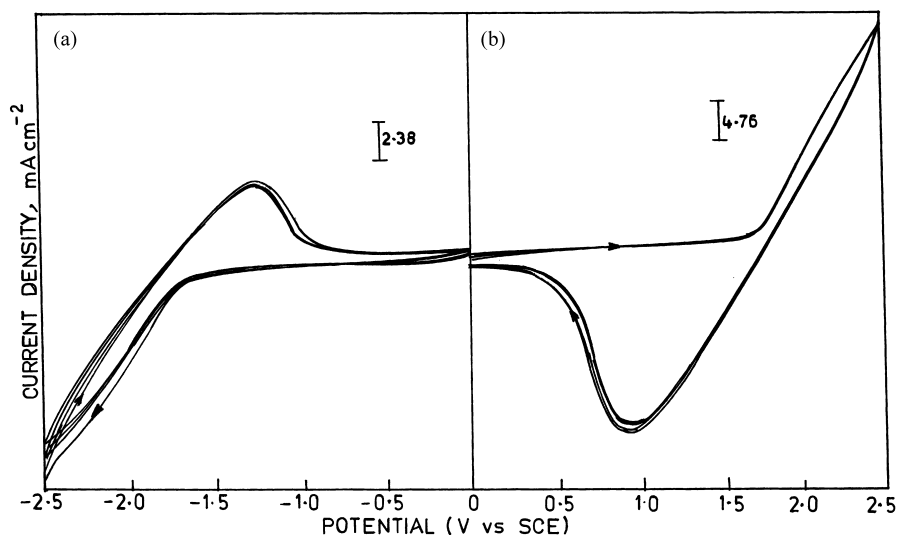

Fig. 1. Multisweep cyclic voltammograms for 0.25 M $LiClO_4$ in PC medium with CPP graphite: (a) reductive intercalation of Li$^+$ ions; (b) oxidative intercalation of ClO_4^- ions. Sweep rate = 40 mV s^{-1}.

Table 1
Cyclic voltammetric data for ClO_4^- intercalation/de-intercalation on CPP electrodes in 0.25 M $LiClO_4$ containing different solvents/solvent mixtures at 40 mV s^{-1}

No.	Solvent/solvent mixture	E_{th} (V)	DPP (V)	ΔE (V)	Q_{in} (mC cm^{-2})	Q_{de} (mC cm^{-2})	(Q_{de}/Q_{in}) = IDE (%)
1	PC (0.25 M)[a]	1.76	1.04	0.72	445.56	315.56	0.70
2	PC (0.5 M)	1.96	1.26	0.70	379.50	284.51	0.75
3	AN	1.86	1.30	0.56	909.64	536.21	0.59
4	Sulfolane	1.96	1.42	0.54	154.33	74.52	0.48
5	EC/sulfolane[b]	2.00	1.48	0.52	90.85	59.80	0.66
6	EC/DEC	1.80	1.12	0.68	216.66	18.68	0.55
7	PC/DEC	1.70	1.08	0.90	254.70	133.70	0.52
8	PC/sulfolane	1.94	1.04	0.90	212.75	106.26	0.50
9	DEC/sulfolane	1.90	0.94	1.00	191.59	90.39	0.49

[a] At 3 mV s^{-1}, Q_{in} = 4534.3 mC cm^{-2}, Q_{de} = 1795.3 mC cm^{-2}, IDE = 40.0%.
[b] At 3 mV s^{-1}, Q_{in} = 3348.0 mC cm^{-2}, Q_{de} = 1397.2 mC cm^{-2}, IDE = 41.7%.

Table 2
Cyclic voltammetric data for Li^+ intercalation/de-intercalation processes on CPP electrodes in 0.25 M $LiClO_4$ containing different solvents and solvent mixtures at 40 mV s^{-1}

No.	Solvent/solvent mixture	E_{th} (V)	DPP (V)	ΔE (V)	Q_{in} (mC cm^{-2})	Q_{de} (mC cm^{-2})	(Q_{de}/Q_{in}) = IDE (%)
1	PC (0.25M)[a]	−1.68	−1.26	0.42	179.21	59.86	0.33
2	PC (0.5M)	−1.78	−1.40	0.38	140.18	53.31	0.39
3	DME	−2.00	−1.56	0.44	81.16	26.30	0.33
4	Sulfolane	−1.92	−1.62	0.30	83.34	15.72	0.20
5	PC/DME[b]	−1.94	−1.48	0.46	249.54	69.87	0.30
6	EC/DME	−2.02	−1.86	0.16	183.50	17.49	0.10

[a] At 3 mV s^{-1}, Q_{in} = 1602.5 mC cm^{-2}, Q_{de} = 239.5 mC cm^{-2}, IDE = 15.0%.
[b] At 3 mV s^{-1}, Q_{in} = 1827.0 mC cm^{-2}, Q_{de} = 318.8 mC cm^{-2}, IDE = 17.5%.

calation process is totally absent in the single solvents EC, AN, DEC and in their binary combinations. In general, for comparison of the solvent and solvent mixtures, 0.25 M $LiClO_4$ was used. If the solubility of $LiClO_4$ is higher in specific solvents or solvent mixtures, then the IDE can be improved considerably. A few experiments with a higher $LiClO_4$ concentration of 0.5 M are also presented in Tables 1 and 2.

Some cyclic voltammetric studies were also carried out to evaluate the IDE of Li^+ and ClO_4^- ions in selected solvents and solvent mixtures such as PC, PC/DME and EC/sulfolane at a slow sweep rate of 3 mV s^{-1}. The IDE of ClO_4^- ions is found to be very low in both PC and EC/sulfolane (about 40%) compared to the value obtained at 40 mV s^{-1} (Table 1). The same trend is found for Li^+ ions (Table 2). This may be due to the fact that at higher sweep rate, the total quantity of
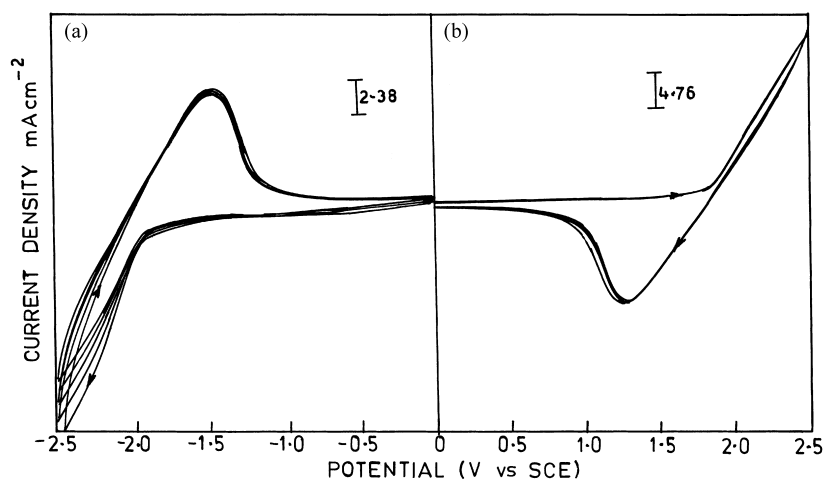

Fig. 2. Multisweep cyclic voltammograms for 0.25 M $LiClO_4$ in PC/DME medium with CPP graphite: (a) reductive intercalation of Li^+ ions; (b) oxidative intercalation of ClO_4^- ions. Sweep rate = 40 mV s^{-1}.
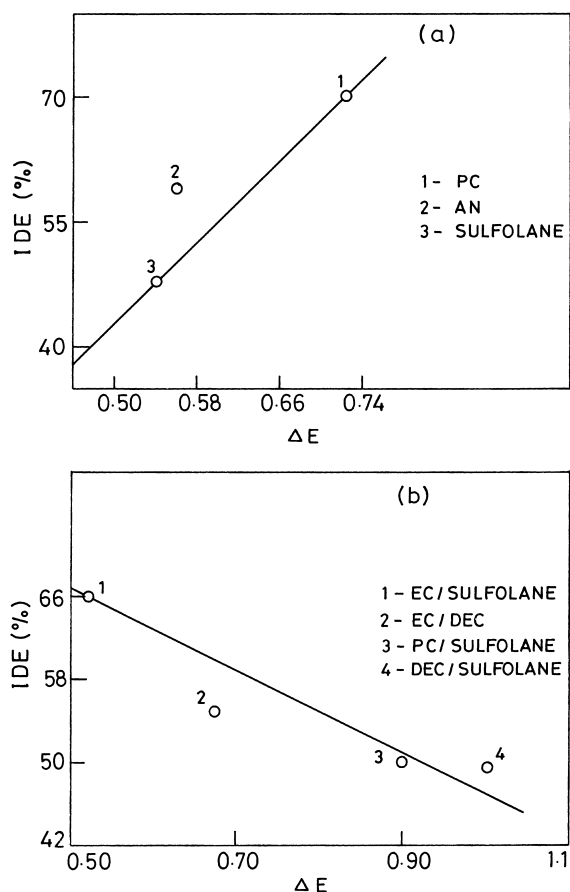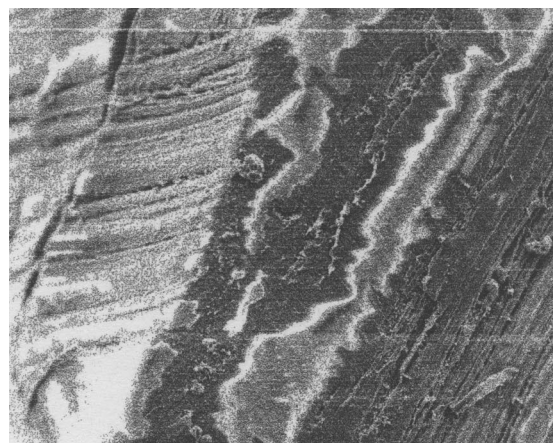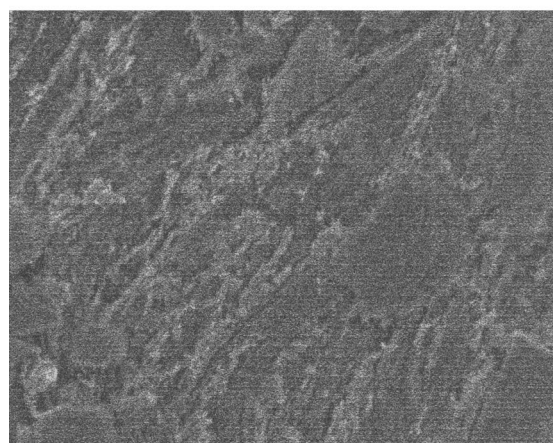
(a)

(b)

Fig. 3. ClO_4^- ions intercalation/de-intercalation efficiency vs. ΔE (E_{th} DPP) of 0.25 M $LiClO_4$ in: (a) single solvents; (b) solvent mixtures with CPP graphite at 40 mV s^{-1}.

Fig. 4. Scanning electron micrograph of CPP electrode with ClO_4^- intercalated/de-intercalated in (a) PC × 100; (b) EC/sulfolane × 250 at 3 mV s^{-1}.

ions entering into the graphite lattice is lower and the depth of insertion of the ionic species in the graphite lattice is much lower. Hence, the surface-bound intercalents can de-intercalated efficiently and give rise to higher IDE values.

The following specific observations relating to solvent effects on the IDE especially with respect to anionic species, deserves special mention. When single solvents are employed, the IDE is found to decrease with increasing threshold potential (E_{th}) for the intercalation process and there is a decreasing difference between E_{th} and DPP (ΔE), as shown in Table 1 (No. 1–4). In the case of these single solvents, the lower threshold potential for intercalation should lead to less competition from other background processes, and hence higher IDE. The opposite trend is observed in the case of a mixed-solvent system (Table 1, No. 5–9). In this case, the IDE is found to be higher when E_{th} is considerably higher. This contrasting trend is illustrated in Fig. 3(a) and (b). It appears that in the case of single solvents, the anionic species is intercalated with a larger number of the solvent molecules, whereas in the mixed solvent system solvent-free anionic species or anionic species with much lower number of co-solvents is intercalated into the graphite lattice at more positive potentials. Although E_{th} is thus higher, this process would lead to less exfoliation of the

graphite lattice and, hence, to reversible de-intercalation. Scanning electron microscopic studies also lend support to this view.

The substantial morphological change and exfoliation of graphite lattices after a single intercalation/de-intercalation cycle is shown in Fig. 4(a). By contrast, Fig. 4(b) shows that the surface morphological changes in the case of a mixed-solvent system are substantially less. This trend lends further support to the view expressed above. In the case of a single solvent, some solvated ionic species of considerably higher size are intercalated into the graphite lattice and thus the surface exfoliation and damage appears to be higher. In the case of a mixed-solvent system, solvent-free or less-solvated anionic species are intercalated at a more positive threshold potential (E_{th}). However, since co-solvent intercalation is lower, graphite exfoliation and surface deterioration are at a minimum. Two earlier reports support this observation. In the case of Li^+ ion intercalation in PC, addition of 5% ethylene sulfite [15] and propylene sulfite [16] were found to improve the IDE. Compared with PC, intercalation of Li ions in trifluoro PC solvent is lower although with lower efficiency [7].

4. Conclusions

For the polypropylene composite graphite electrodes employed as the host lattice in the present investigation, anionic intercalation is more efficient than cationic intercalation. Increased intercalation/de-intercalation leads to extensive graphite exfoliation and irreversible surface transformation. Though mixed solvents do not enhance the intercalation/de-intercalation efficiency, it reduces graphite exfoliation probably due to a much lower level of co-solvent uptake during intercalation. From this point of view, a mixed-solvent system offers greater scope for further investigation, with special reference to increased cycle-life of intercalation-based battery systems.

References

[1] M. Noel, R. Santhanam, J. Power Sources 72 (1998) 53.

[2] D. Aurbach, B. Markovsky, I. Weissman, E. Levi, Y. Ein-Eli, Electrochim. Acta 45 (1999) 67.

[3] Y. Ein-Eli, B. Markovsky, D. Aurbach, Y. Carmeli, H. Yamin, S. Luski, Electrochim. Acta 39 (1994) 2559.

[4] C.R. Yang, Y.Y. Wang, C.C. Wan, J. Power Sources 72 (1998) 66.

[5] C. Wang, H. Nakamura, H. Komatsu, M. Yoshio, H. Yoshitaka, J. Power Sources 74 (1998) 142.

[6] Y. Ein-Eli, S.F. McDevitt, D. Aurbach, B. Markovsky, A. Schechter, J. Electrochem. Soc. 144 (1997) 180.

[7] M. Inaba, Y. Kawatate, A. Funabiki, S.K. Jeong, T. Abe, Z. Ogumi, Electrochim. Acta 45 (1999) 99.

[8] K. Hayashi, Y. Nemoto, B. Tobishima, J. Yamaki, Electrochim. Acta 44 (1999) 2337.

[9] A.M. Christie, L. Christie, C.A. Vincent, J. Power Sources 74 (1998) 77.

[10] A.D. Pasquier, F. Disma, T. Bowmer, A.S. Gosdz, C. Amatucci, J.M. Tarascon, J. Electrochem. Soc. 145 (1998) 472.

[11] S. Mori, H. Asahina, H. Suzuki, A. Yohei, K. Yokoto, J. Power Sources 68 (1997) 59.

[12] M. Ishikawa, M. Morita, M. Asao, Y. Matsuda, Electrochim. Acta 141 (1994) 1105.

[13] C. Yuqun, L. Hong, W. Lie, L. Tianhong, J. Power Sources 68 (1997) 187.

[14] G.C. Chung, S.H. Jun, K.Y. Lee, M.H. Kim, J. Electrochem. Soc. 146 (1999) 1664.

[15] G.H. Wrodnigg, J.O. Besenhard, M. Winter, J. Electrochem. Soc. 146 (1999) 470.

[16] G.H. Wrodnigg, T.M. Wrodnigg, J.O. Besenhard, M. Winter, Electrochem. Commun. 1 (1999) 148.

[17] R.T. Carlin, H.C. Delong, J. Fuller, P.C. Trulove, J. Electrochem Soc. 141 (1994) L 73.

[18] R. Santhanam, M. Noel, J. Power Sources 56 (1995) 101.

[19] R. Santhanam, M. Noel, J. Power Sources 76 (1998) 147.

[20] R. Santhanam, M. Noel, J. Power Sources 66 (1997) 47.

[21] R. Santhanam, M. Noel, J. Power Sources 63 (1996) 1.