Short Communication

Electrochemical intercalation of ionic species of tetrabutylammonium perchlorate on graphite electrodes. A potential dual-intercalation battery system

R. Santhanam, M. Noel

Central Electrochemical Research Institute, Karaikudi 623 006, India

Abstract

A study is conducted on the intercalation of ionic species of tetrabutylammonium perchlorate in propylene carbonate medium in order to develop a dual-intercalation battery system. Cyclic voltammetry, current–time transients, X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements are carried out to establish and evaluate the efficiency of intercalation of perchlorate anion and tetrabutylammonium cation. Dual intercalation for both the ionic species can indeed be achieved from the same solvent. Compared with high purity commercial graphite material, a graphite polypropylene composite electrode containing 20 wt.% polypropylene as a binder (CPP) is found to be more efficient. The intercalation/de-intercalation efficiency increases with electrolyte concentration and reaches up to 55% on this CPP material for both the ionic species. XRD data also confirm the intercalation of both the ions. SEM studies indicate stronger graphite exfoliation during cationic intercalation. Cycling efficiency remains fairly high, however, as long as the intercalation/de-intercalation time does not exceed 10 min.

Keywords: Electrodes; Graphite; Tetrabutylammonium perchlorate; Intercalation

1. Introduction

It is well known that a number of cations, as well as anions, can be electrochemically intercalated into graphite electrodes, as determined by the solvent-supporting electrolyte system that is employed. Perchlorate anions, for example, can be reversibly intercalated from strong aqueous acidic solutions [1,2], or from aprotic solvents such as propylene carbonate (PC) [3–6] and acetonitrile [6], i.e.:

$$nC + ClO_4^- \rightleftharpoons C_n^+ ClO_4^- + e^- \tag{1}$$
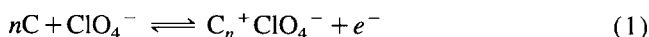
Cationic intercalation cannot be accomplished in aqueous solutions on graphite electrodes because of the competitive hydrogen evolution reaction. Nevertheless, the reversible intercalation of tetrabutylammonium cations (TBA$^+$) has been reported [7–10] in aprotic solvents that have high donor numbers, such as dimethyl sulfoxide and dimethylformamide, i.e.:

$$nC + TBA^+ + e^- \rightleftharpoons C_n^- TBA^+ \tag{2}$$
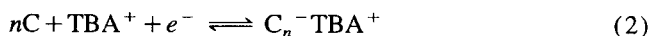
To date, the simultaneous intercalation of both these anions and cations in a single solvent system has still to be accomplished.

Current research efforts into the development of 'rocking-chair' types of batteries attempt to use the same intercalating Li$^+$ ion and two different electrode substrates that act as the anode and the cathode materials (the anode is a Li–carbon intercalation compound, while the cathode is a transition metal oxide such as CoO$_2$, NiO$_2$ or Mn$_2$O$_4$, [11,12]. An alternative strategy is to look for a solvent-supporting electrolyte system that enables the intercalation of the cationic and anionic species of the same supporting electrolyte on the same graphite substrate. The search for such a system has been undertaken recently in the authors' laboratory. Even more recently, a dual-intercalating molten electrolyte battery system, involving organic salts, has been reported [13]. The present work is concerned with the intercalation of tetrabutylammonium perchlorate (TBAP) ionic species in a PC medium. This appears to be an interesting candidate for dual-intercalating battery systems.

2. Experimental

Two varieties of graphite, embedded in Teflon roads, were used for the working electrodes, namely, high purity com-

mercial graphite of 5 mm diameter (HPC grade, Graphite India, Ltd., India) and CPP electrode of 3 mm diameter (containing 80 wt.% natural graphite flakes and 20 wt.% polypropylene as a binder). A platinum foil and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. Dried TBAP and distilled PC were used as the supporting electrolyte and the solvent, respectively.

Cyclic voltammetry (CV) and current–time transient (i–t) measurements, were performed with a potentiostat (Wenking Laboratory Model LB75L), a voltage scan generator (Wenking Model VS672), and an X–Y–T recorder (Rikadenki Model RW-201T). A JEOL (Model 30CF) scanning electron microscope (SEM) was used to examine the intercalated electrodes. X-ray diffraction (XRD) measurements were carried out with a JEOL (Model JDX-3080) X-ray diffractometer.

3. Results and discussion

Typical anodic and cathodic CV responses of a HPC graphite electrode in PC solution containing 0.65 M TBAP at a sweep rate of 40 mV s^{-1} are presented in Fig. 1(a) and (b), respectively. The data show that intercalation/de-intercalation processes occur for ClO$_4$$^-$ anions during the anodic sweep (Fig. 1(a)), and for TBA$^+$ cations during the cathodic sweep (Fig. 1(b)). The voltammetric responses are quite similar to those reported for ClO$_4$$^-$ anions [5,6] and TBA$^+$ cations [10] in different solvent-supporting electrolyte systems. The charge Q_a for anion intercalation and Q_c for cation intercalation (as well as the respective de-intercalation charges) were obtained by integration of the CV responses. The values obtained for HPC graphite (Table 1) indicate that the charge recovery ratio (Q_c/Q_a for anion and Q_a/Q_c for cation) is quite low for both anionic and cationic intercalation. Interestingly, the charge recovery ratio decreases with increasing concentration of the intercalating salt species.

The charge/discharge behaviour was also evaluated in terms of potentiostatic i–t transient measurements. For anionic species, intercalation was carried out at +2.5 V while de-intercalation was performed at +1.4 V. For cationic species, intercalation was undertaken at −2.5 V and de-intercalation at −1.5 V. All the intercalation and de-intercalation processes were carried out for a constant period of 60 s. The charge recovery ratios by this technique are also listed in Table 1. A slightly better recovery is noticed in this technique that involves fairly long time scales. Nevertheless, the overall response is still very poor. During longer periods of potentiostatic polarization (> 10 min), the HPC material was found to disintegrate.

Further experiments were conducted to determine whether graphite polymer composite materials exhibit better performance in the dual-intercalation process. Typical CV responses are presented in Fig. 2(a) and (b) for ClO$_4$$^-$ anions and TBA$^+$ cations, respectively. The results suggest that the inter-
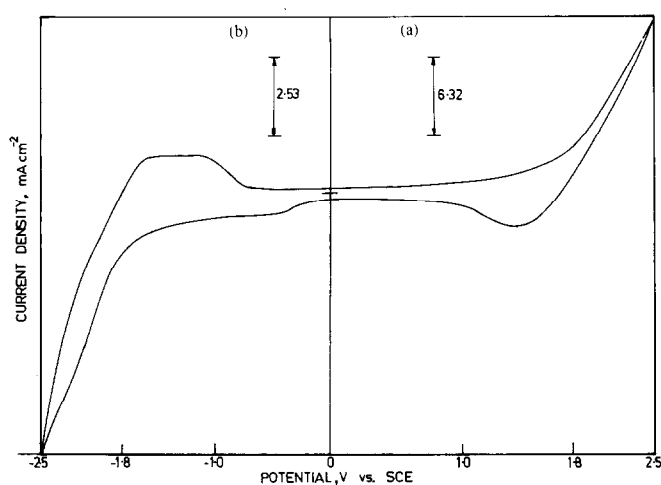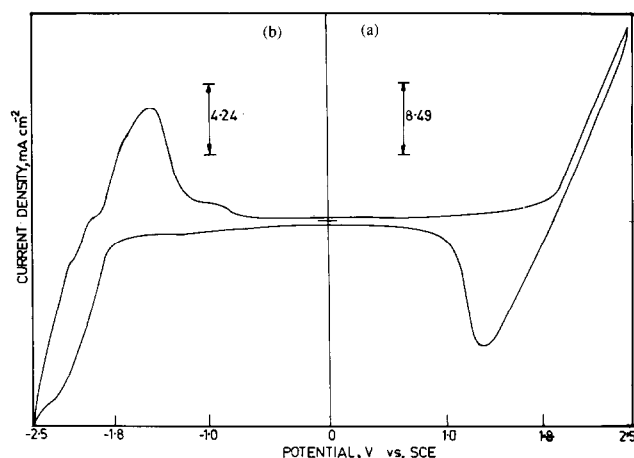

Fig. 1. Cyclic voltammograms for 0.65 M TBAP in PC medium with HPC graphite: (a) oxidative intercalation of ClO$_4$$^-$, and (b) reductive intercalation of TBA$^+$. Sweep rate = 40 mV s^{-1}.

Fig. 2. Cyclic voltammograms for 0.65 M TBAP in PC medium with CPP graphite: (a) oxidative intercalation of ClO$_4$$^-$, and (b) reductive intercalation of TBA$^+$. Sweep rate = 40 mV s^{-1}.
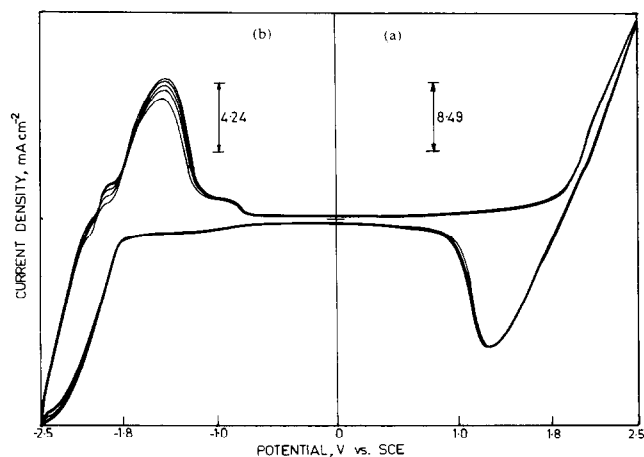

Fig. 3. Multi-sweep cyclic voltammograms for 0.65 M TBAP in PC medium with CPP graphite: (a) oxidative intercalation of ClO$_4$$^-$, and (b) reductive intercalation of TBA$^+$. Sweep rate = 40 mV s^{-1}.

Table 1
Intercalation and de-intercalation charges and their ratios (from cyclic voltammetry and current–time measurements in TBAP–PC solution)

Graphite electrode	Methods	TBAP concentration (M)	Charge (mC cm^{-2}) TBA$^+$, cathodic limit −2.5 V			ClO$_4^-$, anodic limit, +2.5 V		
			Q_c	Q_a	Q_a/Q_c	Q_a	Q_c	Q_c/Q_a
HPC	CV	0.25	50.39	15.27	0.30	133.77	31.85	0.24
		0.65	107.10	21.63	0.20	178.48	24.23	0.14
	i–t	0.25	219.04	76.41	0.35	496.67	119.71	0.24
		0.65	395.93	105.30	0.27	726.57	126.36	0.17
CPP	CV	0.25	80.95	43.13	0.53	262.60	91.91	0.35
		0.65	147.06	83.43	0.57	325.22	183.82	0.57
	i–t	0.25	299.82	141.43	0.47	792.06	282.08	0.36
		0.65	601.12	318.24	0.52	1272.96	650.62	0.51

Table 2
Intercalation and de-intercalation charges and their ratios for CPP electrode at different cathodic and anodic limits (from cyclic voltammetry measurements in 0.25 M TBAP–PC solution)

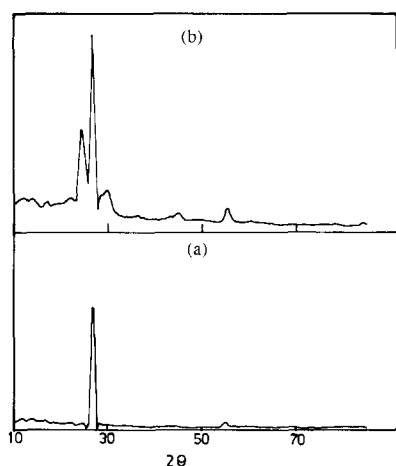| Cathodic potential limits (V)	Charge (mC cm^{-2}) TBA$^+$			Anodic potential limit (V)	ClO$_4^-$		
	Q_c	Q_a	Q_a/Q_c		Q_a	Q_c	Q_c/Q_a
−2.2	35.35	8.48	0.24	+2.2	84.84	25.45	0.30
−2.4	63.63	26.16	0.41	+2.4	221.00	70.70	0.32
−2.5	80.95	43.13	0.53	+2.5	262.60	91.91	0.35
−2.6	113.12	43.83	0.39	+2.6	395.92	127.26	0.32
−2.8	188.06	60.80	0.32	+2.8	633.80	183.82	0.29

Fig. 4. X-ray diffraction patterns for CPP graphite: (a) fresh and (b) polarized cathodically at −2.5 V for 15 min in 0.65 M TBAP–PC solution.

calation/de-intercalation efficiency improves on this CPP electrode in comparison with HPC material. The charge recovery ratios obtained from CV and i–t measurements are summarized in Table 1. In this case, the reversibility exceeds 55%. The intercalation/de-intercalation efficiency increases with increase in the concentration of the supporting electro-

lyte. The latter improvement is greater for ClO$_4^-$ anion intercalation, i.e., from 35 to 56%.

The CPP electrodes exhibit good stability during charge/discharge cycling; typical multi-sweep CV responses are shown in Fig. 3. The reversibility during anion intercalation is close to 100% (Fig. 3(a)). For cation intercalation, the cathodic charge decreases slightly with sweep number, while the anodic charge increases slightly (Fig. 3(b)).

The CV experiments were also performed with different anodic potential limits for anion intercalation and with different cathodic potential limits for cation intercalation to evaluate the effect of the intercalating potential limit on the charge recovery ratio. The results from these experiments are summarized in Table 2. The data indicate that best intercalation/de-intercalation efficiencies are achieved at around + 2.5 and − 2.5 V for anionic and cationic intercalation, respectively.

Anionic as well as cationic intercalation was confirmed by XRD analysis. Typical XRD responses for the CPP electrode before and after intercalation at − 2.5 V for 15 min are presented in Fig. 4(a) and (b), respectively. A distinct XRD peak with a 'd' value of 3.66 Å appears after intercalation of TBA$^+$ cations. A similar intercalation response was also observed for ClO$_4^-$ anions in a PC medium. The XRD
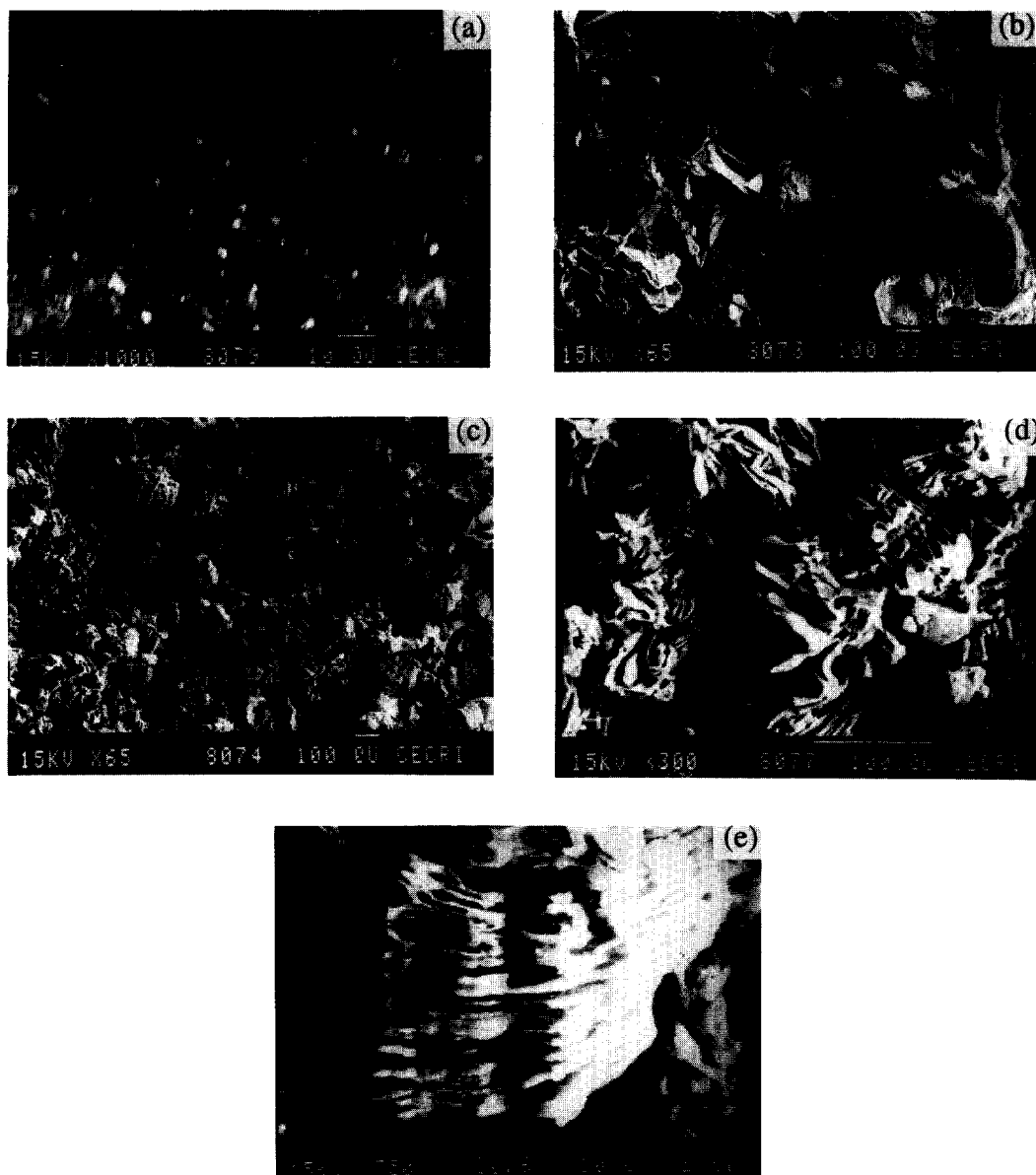
Fig. 5. Electron micrographs of CPP graphite material. (a) fresh, ×1000; (b) TBA⁺ intercalated, ×65; ClO_4^- intercalated: (c) ×65, (d) ×300, and (e) ×750. Polarisation time = 10 min.

response was quite similar to those reported for the same anionic species in the same medium [3,4].

Surface transformations during intercalation were examined by SEM. Typical micrographs for the CPP electrode at a fairly high magnification (×1000) indicate the presence of a uniform smooth surface. The polymeric and graphite regions, however, are visible as distinct zones (Fig. 5(a). Intercalation of cations as well as anions on to a CPP graphite substrate for 10 min leads to significant changes in the surface morphology. Electron micrographs after cation (TBA⁺) and anion (ClO_4^-) intercalation are compared in Fig. 5(b) and 5(c). After cation intercalation the graphite electrode becomes quite rough. Nevertheless, the plate-like structures and exfoliated graphite faces are still visible, and, therefore, confirm cation intercalation (Fig. 5(b)). During anion inter-

calation, however, the electrode surface remains reasonably smooth and uniform (Fig. 5(c)). The intercalated graphite layers are also quite distinctly seen on this surface. Some interesting exfoliated graphite structures are shown in Fig. 5(d) and (e). All these observations lend further support to dual intercalation of the ionic species of TBAP on graphite electrodes in PC medium.

4. Conclusions

The present investigations clearly indicates the possibility of developing a battery system based on dual intercalation of TBA⁺ cations and ClO_4^- anions. A considerable amount of further work is, of course, necessary to raise the charge recov-

ery ratios to acceptable values. This may be achieved by better choice of electrode material or by employing mixed solvent systems or additives. Work in these areas is in progress.

An even more important conclusion may be drawn from this study. It is indeed possible to identify proper solvent-supporting electrolyte systems with appropriate cationic and anionic species to ensure dual intercalation in aprotic solvents themselves. This will open up a large area for further research to evolve even more efficient dual-intercalation systems.

Acknowledgements

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