

Studies of carbon as negative electrode materials for secondary lithium batteries

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Abstract

A number of carbon materials was investigated as lithium storage anodes. The discharge/charge characteristics of the carbon anodes and its dependence on solvents were evaluated. The results from this study demonstrated that pyrolytic and carbon coke carbon in a mixed solvent of propylene carbonate (PC) + dimethoxyethane (DME) have high discharge/charge capacity, superior cycling efficiency and good rechargeability, suitable for use as lithium intercalating negatives in lithium ion cells.

Introduction

The two major problems that severely prevent the wide acceptance and practical use of secondary lithium batteries are their insufficient cycleability and safety. Many efforts have been attempted to overcome these problems, such as the use of alloy anode [1], selection of electrolyte composition [2] or use of chemical shuttles to prevent overdischarge [3]. However, the improvement in the cycle life and especially the safety of the cell is still not satisfactory. In recent years the use of Li storage carbon as anode has been investigated [4-7]. Since with carbon electrode only the process of reversible intercalation-deintercalation of Li cation takes place during cycling, it is expected that the cycleability and safety of the cells may be significantly improved. In this study, we compared the charge/discharge characteristics of a variety of carbon materials for use as Li storage anode and the effects of organic solvents on the intercalation properties of carbon electrode.

Experimental

Graphite (GC, Shanghai), activated carbon (AcC, Hunan) and acetylene black (AbC, Jilin) were all used as-received. The pyrolytic carbon (PyC) was prepared basically according to ref. 5, by vapor phase decomposition of benzene in an argon-filled silica tube at 1050 °C. The coke carbon (CC) was made by heating coal powder at 2000 °C for more than 5 h under protection of argon atmosphere. The carbon electrode used were all polytetrafluoroethylene (PTFE) (15 wt.%) bonded carbon sheets of about 0.25 mm thick, pressed on nickel screen. The laboratory cell consisted of a Li disk (diameter: 15 mm, thickness: 0.06 mm) and a carbon electrode separated by Celgard 2400 separator, that housed together on a PTFE cell. A small piece of Li foil was used as reference electrode. The electrolytes were all 1.0 M LiClO₄ dissolved in propylene carbonate (PC), dimethoxyethane (DME), tetrahydrofuran (THF) and

2-methyltetrahydrofuran (2-MeTHF). The charge/discharge properties of the carbon electrodes were evaluated by constant current cycling with lower cutoff voltages of 0.0 V versus Li reference to avoid Li deposition. The microelectrode of carbon powder was fabricated by filling the carbon powder into the microhole on the tip of a platinum microelectrode which was formed by boiling the glass-sealed microelectrode in diluted $\text{HNO}_3 + \text{HCl}$ solution (1:3).

Results and discussion

Figure 1 shows the first two cycles of discharge/charge curves of various carbon electrodes in 1.0 M $\text{LiClO}_4 + \text{PC}$ and Table 1 summarizes their cycling characteristics. During the first discharge, the carbon electrodes are intercalated with Li to form Li_xC_6 , and their charge/discharge capacities at subsequent cycles represent the available Li storage capacities. It can be seen from the data that the discharge/charge properties of the carbons vary dramatically with the nature of the carbon materials. An AcC electrode had almost no Li storage capacity. Its open-circuit voltage (OCV) recovered rapidly after discharge to 0 V. GC electrode did exhibit certain Li storage ability but its available capacity (~ 30 mA h/g) and coulombic efficiency ($\sim 30\%$) was too low for practical use. On the other hand, electrodes made from AbC, PyC and CC all showed excellent reversibility for Li intercalation with coulombic efficiency above 90% since the second cycle and their reversible capacities exceeded 190 mA h/g at moderately high rate of 30 mA h/g (Table 1). Figure 2 gives the X-ray diffraction (XRD) patterns of the three types of carbon PyC, CC and AbC. A general structural feature of these

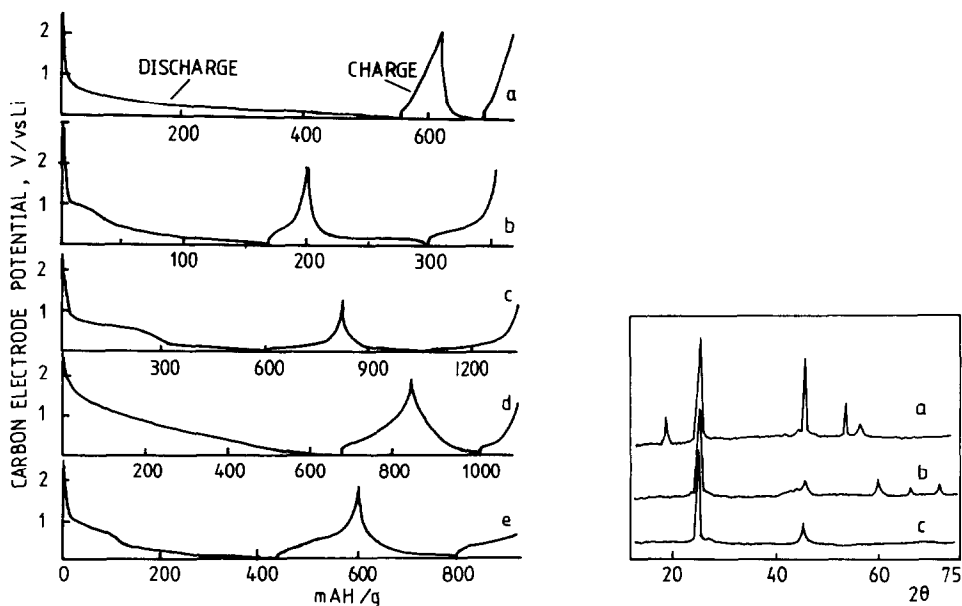


Fig. 1. The first two discharge/charge profiles of carbon electrode: (a) AcC; (b) GC; (c) PyC; (d) AbC, and (e) CC in 1.0 M LiClO_4/PC .

Fig. 2. X-ray diffractograms of the carbon materials: (a) PyC; (b) CC, and (c) AbC.

TABLE 1

The discharge/charge characteristics of various carbon electrodes in 1.0 M LiClO₄/propylene carbonate

	GC	AcC	CC	AbC	PyC	
	$I_d=I_c$ (mA/g)	40	36	10	34	30
	V_d , cutoff (V)	0.02	0.02	0	0.02	0.01
	V_c , cutoff (V)	2.0	2.0	1.5	1.5	1.0
First cycle	C_d (mA h/g)	170	550	570	680	480–500
	C_c (mA h/g)	30	70	185	170	230–250
	η_{cd} (%)	18	12.7	32	25	40–50
Second cycle	C_d (mA h/g)	100	100	185	200	250
	C_c (mA h/g)	50	14	175	190	237
	η_{cd} (%)	50		94	95	95
Cycle number achieved			65	120	150	

I_d , V_d and C_d : discharging current, voltage and capacity; I_c , V_c and C_c : charging current, voltage and capacity; η_{cd} : charge/discharge capacity efficiency.

materials is their very similar interplanar spacing with $d(002)$ values inbetween 3.5–3.4 Å. This could probably be the structural requirement of carbons for Li insertion.

One problem, that was always observed for all the carbon electrodes, is the low coulombic efficiency at the first discharge/charge cycle in PC electrolyte. This phenomenon has been considered to arise from the electroreduction of PC electrolyte to form a surface passivating film and the irreversible intercalation of Li into graphite structure [8, 9]. Our IR analysis of the cycled carbon electrode showed three distinctive bands at 1516, 1441 and 503 cm^{-1} agreed with the IR absorption of Li₂CO₃ (1490, 1430 and 490 cm^{-1}), and X-ray photoelectron spectroscopy (XPS) spectra of the discharged electrodes showed a strong new band at 289.7 eV which is characteristic of CO₃²⁻ or HCO₃⁻. All the spectroscopic evidences obtained in our experiments suggest that PC reduction is the main cause for the observed irreversible capacity loss at the first cycle. This problem may result in a difficulty in the design of practical Li ion cells because of a great excess of Li needed to be loaded in cathode for compensating the irreversible electrical consumption. Thus, it is of practical importance to select appropriate solvents that have less electroreductive activity and less reaction ability with Li carbon intercalate.

Figure 3 shows the first two cycling curves of a PyC electrode in PC, DME, 2-MeTHF and THF. A great difference in the cycling properties can be seen for the carbon electrode in these solvents. In PC electrolyte, the coulombic efficiency at first discharge/charge was only about 40%, whereas in DME, 2-MeTHE and THF the initial coulombic efficiency may exceed 60%. Furthermore, the discharge and charge capacity of the electrode in 2-MeTHF, THF and DME are obviously greater than in PC. Figure 4 compares the voltammograms of a PyC microelectrode in PC, DME and 2-MeTHF. The first reduction band starting at +2.6 V is due to the surface adsorbates because its shape and height vary sensitively with the electrode pretreatment. Two pairs of reduction-oxidation peaks at +1.0/+0.25 and -0.05/0.0 V are evidently characteristic of the intercalation-deintercalation of Li ions and the deposition-anodic dissolution of Li in consistent with previous assignment by Besenhard [10]. In PC

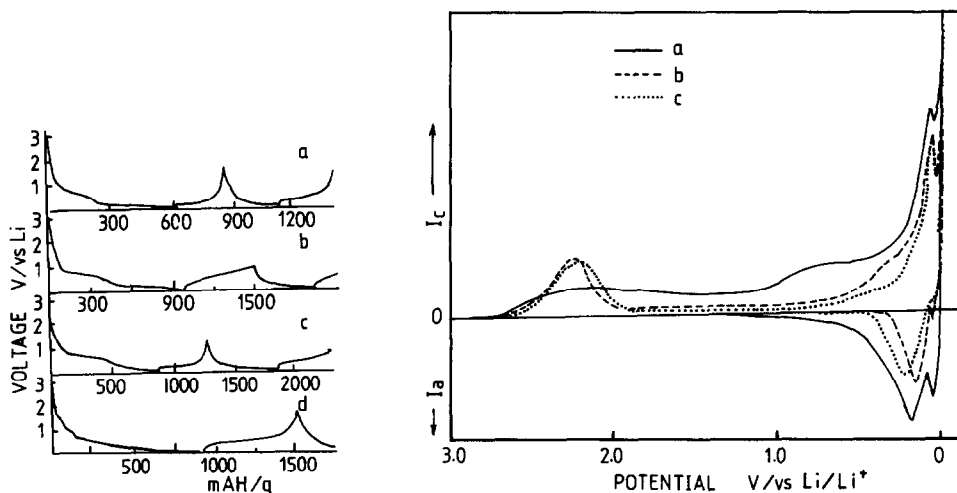


Fig. 3. The discharge/charge curves of a PyC electrode in 1.0 M LiClO_4 in: (a) PC; (b) DME; (c) 2-MeTHF, and (d) THF.

Fig. 4. The first scan voltammograms of PyC microelectrode in 1.0 M LiClO_4 in: (a) PC; (b) DME, and (c) 2-MeTHF.

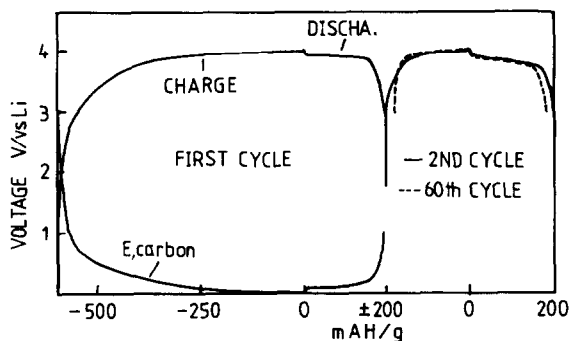


Fig. 5. Charge/discharge curves of the test cell $\text{CC}/1.0 \text{ M LiClO}_4 + \text{PC}/\text{LiCoO}_2$: (a) first, (b) second, and (c) 60th cycle. $I_d = I_c = 0.33 \text{ mA/cm}^2$ (10 mA/g carbon).

electrolyte, there was always a large broad reduction peak observed at +1.5 to 0.25 V at first scan, featuring the electroreduction of the solvent. While in DME and 2-MeTHF the reduction currents of these two solvents were greatly decreased suggesting a sluggish electroreduction of DME and 2-MeTHF on the carbon surface. This may be the reason for the observed higher coulombic efficiency of the carbon electrode in 2-MeTHF and DME than in PC at first cycle. However, from the standard of long-term cycleability and performance characteristics, we considered that the mixture of PC and DME (50%:50%) is still a best choice of the electrolyte for Li storage carbon anode.

The charge/discharge curves of $\text{PyC}/\text{Li}_x\text{CoO}_2$ and $\text{CC}/\text{Li}_x\text{CoO}_2$ are shown in Figs. 5 and 6. Both of the test cells exhibited high voltage, flatter working voltage profile

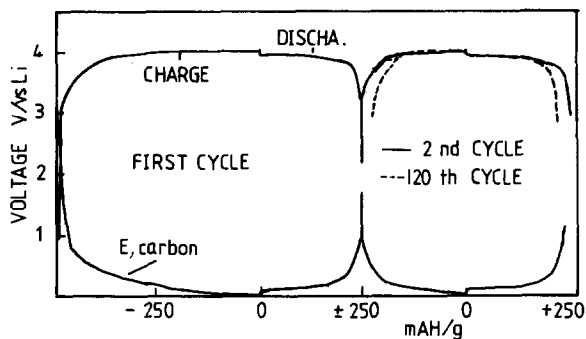


Fig. 6. Charge/discharge curves of the test cell PyC/1.0 M LiClO₄+PC/Li₂CoO₂: (a) first, (b) second, and (c) 120th cycle. $I_d=I_c=0.5$ mA/cm² (30 mA/g carbon).

and good cycleability, showing a great promise for construction of practical rechargeable cells.

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