Cokes as negative electrodes in secondary batteries

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Abstract

The lithium intercalated carbons (Li_xC_6) have replaced the metallic lithium negative electrodes in secondary lithium batteries. In order to improve high energy density and long cycle life, it is necessary to find those carbonaceous materials that have an excellent lithium intercalation and de-intercalation capacity. In this work, the electrochemical behaviour of various cokes in ethylene carbonate (EC) and dimethyl carbonate (DMC) electrolyte were investigated by charge and discharge cycling processes and cyclic voltammetry technique. The petroleum coke (C342) has the highest capacity during cycling and the lowest irreversible capacity loss during the first cycle. Cyclic voltammetry revealed that the cycle efficiencies of three cokes are very high.

Keywords: Negative electrodes; Electrodes; Secondary lithium batteries

1. Introduction

The secondary lithium battery containing a lithium anode has some limitations to cycle-life performance and dendrite problem. Carbon is one of the candidates, to be used in negative electrode materials, that have been able to form lithium intercalation compounds. Moreover, carbons are cheap, nontoxic and have no dendrite problem during the charge and discharge processes. Carbons are now used as anode materials in secondary lithium-ion batteries. The lithium-ion secondary battery has, therefore, a high energy density, long cycle life and excellent safety characteristics.

2. Experimental

The pitch coke (P-coke), needle coke (N-coke) and petroleum coke (C342) were used as the carbon samples. In order to decompose the impurities (such as sulfur and nitrogen), all of the carbonaceous materials had been heat-treated at 1700 °C. These negative electrodes were prepared by mixing coke materials with 3 wt.% Teflon binder, and spread on to the nickel grid to form the carbon electrodes. These positive electrodes were made by using $LiCoO_2$ materials. From the viewpoint of cell capacity, that was regulated by the negative electrode, the amount of active material in the positive electrode is far higher than that in the negative electrode. The electrochemical characterization of various cokes are tested in a 50:50 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC)+1 M $LiClO_4$ electrolyte solution. These tests were galvanostatically cycled at 0.6 mA/cm^2 to 4.2 V cutoff voltage for charge and 0.3 mA/cm^2 to 2.65 V cutoff voltage for discharge. The cyclic voltammetry tests of the carbon electrodes were measured in a three-electrode cell. The lithium metal was used as reference electrode. The scan rate of cyclic voltammetry is 0.5 mV/s. The crystalline parameters of these coke materials were collected by using a high power X-ray diffractometer.

3. Results and discussion

The physical properties and d_{002} spacing crystalline parameters of three cokes are shown in Table 1. The

Table 1
Physical properties of various coke materials

Coke materials	d_{002} (Å)	Density (g/cm^3)	Surface area (m^2/g)	Irreversible capacity loss
P-coke	3.41	2.09	2.3	0.24
N-coke	3.45	2.13	2.6	0.26
C342	3.47	2.15	6.4	0.21

irreversible capacity losses during the first cycle are also shown in Table 1. Petroleum coke (C342) shows the lowest irreversible capacity loss, 0.21. The irreversible capacity losses of P- and N-cokes are 0.24 and 0.26, respectively. Fig. 1 shows the cycle characteristics of discharge capacity of various cokes. It was found that C342 had the highest discharge capacity during cycling. P-coke shows the next discharge capacity, and N-coke the lowest discharge capacity. The cyclic voltammetry curves of three cokes obtained at 25 °C during the cycling is shown in Fig. 2. The positive current represents the lithium de-intercalation process, and the
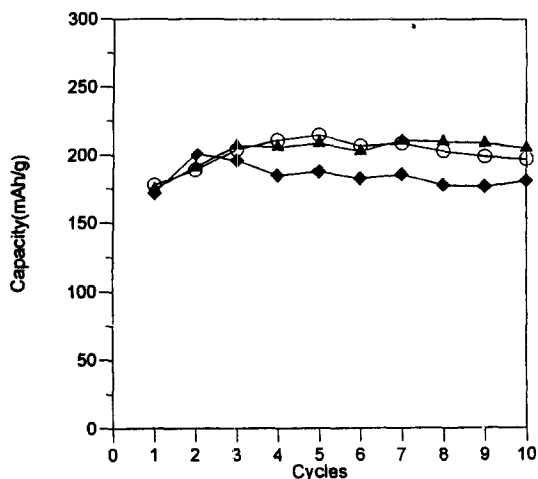

Fig. 1. Variation of the discharge capacity of three coke materials: (O) C342; (▲) P-coke, and (♦) N-coke.
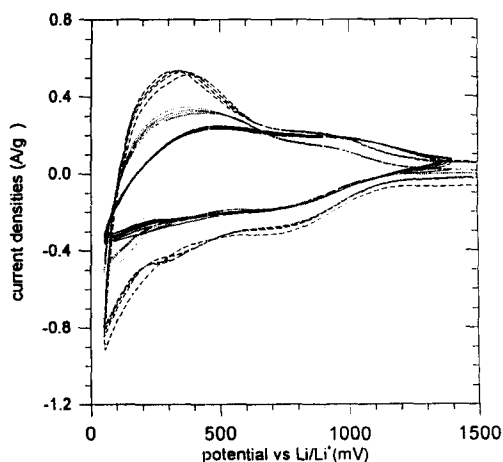

Fig. 2. Cyclic voltammetry for various cokes at a scan rate of 0.5 mV/s: (——) P-coke; (·····) N-coke, and (----) C342.

negative current is the lithium intercalation process. During lithium de-intercalation, two broad peaks are observed around 0.3 and 0.9 V for these three cokes. The petroleum coke (C342) shows a higher ratio of peak current (0.3 V/0.9 V), it means most of the Li^+ ions will be de-intercalated at a lower voltage. For a highly graphitized carbon, its de-intercalation current shows a sharp peak at 0.35 V. The broad current peaks of three cokes therefore reveal their non-graphitized structures. As shown in Fig. 2, lithium intercalates into cokes below 1.1 V, and a plateau-like peak is subsequently observed at 0.8 V. When sweeping to low potential, the intercalation current is increased to 0.2 V; however, no peak is observed even at a potential down to 0.05 V. The cycling capacities during the potential sweeping can be calculated by intergrating current with sweep time. The cycling efficiencies of the three cokes are very high, 98% for P-coke, 99% N-coke and 97% for C342. The decay of the peak currents is not significant and shows good cycling reversibility, which can be proved by charging and discharging tests shown in Fig. 1.

4. Conclusions

The petroleum coke (C342) shows the highest capacity during cycling and the lowest irreversible capacity loss during the first cycle. The discharge capacity of P-coke is higher than that of N-coke and P-coke has a smaller irreversible capacity loss than N-coke. Cyclic voltammetry tests revealed that the cycle efficiencies of the three cokes are very high. The three cokes have, therefore, a good cycling reversibility.

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