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Short Communication

Improving the electrochemical properties of carbon anodes in lithium secondary batteries

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Abstract

The electrochemical properties of carbon anodes in lithium secondary batteries are improved by the addition of vanadium as V_2O_5. The action of the added V_2O_5 is different from that obtained by incorporating a nonmetallic element such as nitrogen, boron, phosphorous or silicon. Because it can increase the distance between the 002 planes of the carbon and act as nucleating agent that promotes the formation of a layer-like carbon structure, V_2O_5, not only enlarges the carbon anode's reversible capacity of lithium storage but also improves the cycling behavior. © 1998 Published by Elsevier Science S.A.

Keywords: Carbon; Anode; Lithium secondary battery; Improving

1. Introduction

It is well known that lithium-ion batteries have many advantages over traditional rechargeable batteries (e.g., nickel/cadmium). These advantages include: high output voltage, light weight, high capacity, freedom from pollution. The usual anode materials are carbons, that are produced by heat-treatment at high temperature. These forms of carbon have two main disadvantages: (i) the need for high temperature; (ii) the reversible capacity for lithium storage is quite limited compared with lithium metal. Accordingly, many attempts have been made to improve the reversible capacity of the carbon anode. These have included, for example, the incorporation of heterogeneous atoms such as nitrogen, boron, phosphorus and silicon [1–4]. Some of these additives have proved to be promising.

In 1994, Sato et al. [5] reported that polymeric carbon prepared at a relative low temperature (800°C) has a high capacity of 680 mA h g^{-1}, i.e., much larger than the theoretical capacity of graphite. Consequently, polymeric carbon has attracted much attention. Most of these carbon electrodes are produced from the heat-treatment of phenol–aldehyde resins [6,7].

The authors reported [8] a new kind of polymeric carbon obtained from the heat-treatment of melamine–aldehyde resin. Its cycling behavior, however, is not satisfactory, i.e., the reversible capacity for lithium storage decreases greatly with increasing cycle number, as is the case with most polymeric carbons. If this problem is not overcome, polymeric carbons will not be practical even though their reversible capacity is large.

This communication reports a new approach, i.e., the addition of the transitional element, vanadium, into the carbon precursor to improve the electrochemical properties of polymeric carbon.

2. Experimental

The preparation of melamine resin and the pyrolysis process were the same as those reported previously [8]. The difference was that vanadium was added as V_2O_5 after the condensation polymerization and then mixed uniformly. The amount of V_2O_5 was a percentage based on the weight of melamine resin. XRD data were obtained with a D/MAX-3B diffractometer, and electron micrographs with a Hitachi S530 scanning electron microscope. The capacity of the carbonaceous materials was measured with lithium metal as the cathode. The anode was prepared from a mixture of carbonaceous material obtained from the above pyrolysis process and 5 wt.% PTFE as binder. The electrolyte was 1 M $LiClO_4$ dissolved in a mixture of DEC

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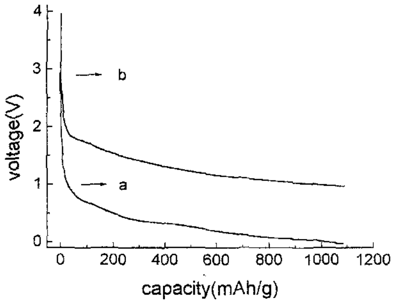

Fig. 1. Discharge (lithium storage) voltage curves of carbon anodes in a lithium secondary battery which uses lithium metal as a cathode. (a) Carbon from heat-treatment of melamine without addition of V_2O_5 at 600°C. (b) Carbon from heat-treatment of melamine with addition of 2 wt.% V_2O_5 at 600°C. Note: In order to discern whether there are any differences between the respective discharging (lithium storage) voltage curves, 1 V is added to all discharge voltages of carbon (b).

and EC (volumetric ratio = 7:3). The discharge (lithium storage) and charge (lithium removal) voltages were between 2.0 and −0.03 V and the current was constantly 20 mA g^{-1}.

3. Results and discussion

3.1. Influence of V_2O_5 on discharge–charge behavior

3.1.1. Reversible capacity on first cycle

As is well known, vanadium pentoxide can be used as the cathode of a lithium-ion battery and can intercalate lithium ions at a high voltage, namely, more than 3.0 V. The data in Fig. 1a,b show that the addition of V_2O_5 causes no apparent change to the discharging voltage (lithium storage) curve. Thus, the effect of the added V_2O_5 on the discharging (lithium storage) curve is negligible.

Table 1
Reversible capacity of prepared carbon anodes in the first cycle of lithium secondary batteries which use lithium metal as cathode

Sample no.	Temperature (°C)	Amount of added V_2O_5	Reversible capacity (mA h g^{-1})
A0	600	0%	536
A1	600	0.5%	587
A2	600	1.0%	584
A3	600	2.0%	559
B0	800	0%	400
B1	800	2.0%	434
B2	800	5.0%	456

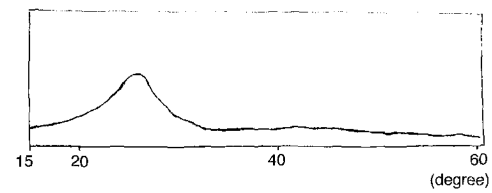

Fig. 2. X-ray diffraction pattern of carbon from polymer with 5 wt.% V_2O_5 and heat-treated at 800°C.

Table 1 shows that the addition of V_2O_5 increases the reversible capacity of lithium storage during the first cycle. At a relatively low temperature (600°C), the reversible capacity reaches its highest value at about 0.5 wt.% V_2O_5. The capacity decreases as the amount of V_2O_5 is increased. At a higher temperature (800°C), however, the increase in capacity is greater than that obtained at 600°C and more V_2O_5 can be added.

3.1.2. Cycling behavior

The added vanadium pentoxide can improve the cycling behavior, see Table 2. When V_2O_5 is added to the melamine–aldehyde resin, the cycling behavior is not significantly improved at the lower temperature (600°C), but is considerably enhanced at higher temperature (800°C). Nevertheless, the results are still not adequate for practical applications. This is possibly due to the fact that the mixture of melamine resin and V_2O_5 is not quite uniform because the mixing process is carried out mechanically between heterogeneous phases. If the dispersion of V_2O_5 can be achieved at the nanometer level, the results may be more satisfactory.

It is concluded, therefore, that the addition of V_2O_5 can improve the discharge–charge properties of the obtained carbon. If the mixing is improved, the carbon can serve as a practical anode for lithium-ion batteries.

3.2. Effect of addition of V_2O_5 on the d_{002} value of carbon

The typical structure of the obtained carbon, as seen from the XRD pattern, is amorphous. The XRD pattern of sample B2 is shown in Fig. 2. The distance between the 002 planes, i.e., the d_{002} value, can be obtained from this pattern; the results are given in Table 3. The d_{002} value

Table 2
Cycling behavior of prepared carbon anodes during the cycling of lithium secondary batteries which use lithium metal as cathode

Sample no.	Temperature (°C)	Amount of added V_2O_5 (wt.%)	1st reversible capacity (mA h g^{-1})	3rd reversible capacity (mA h g^{-1})	5th reversible capacity (mA h g^{-1})
A0	600	0	536	338	303
A2	600	1.0	584	434	333
B0	800	0	400	303	237
B2	800	5.0	456	435	390

Table 3
Effects of V_2O_5 addition on the d_{002} value of the prepared carbon

Amount of added V_2O_5	Temperature (°C)	d_{002} (Å)
0%	600	3.434
1.0%	600	3.452
2.0%	600	3.569

increases with the amount of added V_2O_5. Nevertheless, all the d_{002} values are less than that of the graphite intercalation compound LiC_6, i.e., 3.706 Å [9]. Thus, the higher the d_{002} value, the more easily can lithium ions intercalate into the 002 planes and improve the cycling behavior of the carbon.

3.3. Effect of addition of V_2O_5 on carbon morphology

The morphology of the obtained carbons is presented in Figs. 3 and 4. The carbons with V_2O_5 have a layer-like structure while the carbon without V_2O_5 is mosaic. It has been shown [10] that vanadium can act as a nucleating agent during the heat-treatment of coke. The experiments reported here illustrate that this can lead to the formation

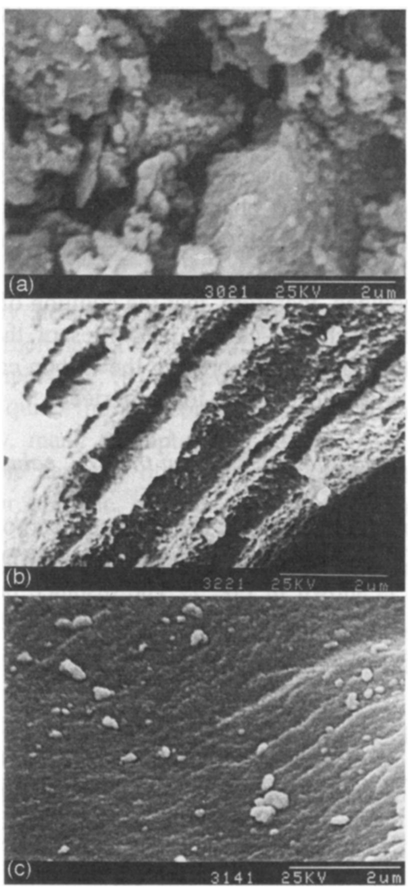

Fig. 3. Electron micrographs of carbons prepared by heat-treatment of melamine–aldehyde resin, with or without the addition of V_2O_5, at 600°C. (a) 0 wt.% V_2O_5. (b) 0.5 wt.% V_2O_5. (c) 2.0 wt.% V_2O_5.

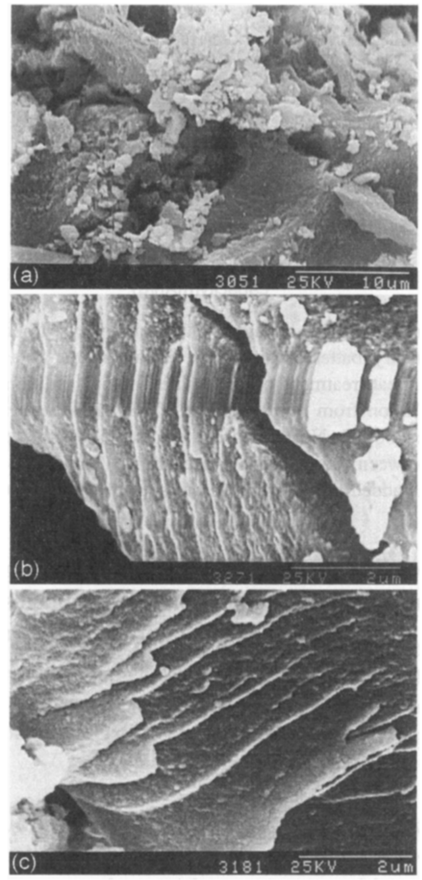

Fig. 4. Electron micrographs of carbons prepared by heat-treatment of melamine–aldehyde resin, with or without the addition of V_2O_5, at 800°C. (a) 0.0 wt.% V_2O_5. (b) 2.0 wt.% V_2O_5. (c) 5.0 wt.% V_2O_5.

of a layer-like structure. Other workers have found [11] that when the structure of carbon has preferred orientation, its performance as the anode in lithium secondary batteries is improved, and that carbon with a layered texture has good charge–discharge characteristics [12]. Therefore, the carbon obtained from the addition of V_2O_5 will display a larger reversible capacity and superior cycle behavior. This conclusion is consistent with the results given in Tables 1 and 2.

From the above discussion, it is seen that the added V_2O_5 can exert appreciable effects on the carbon structure and its action mechanism is quite different from that reported for nonmetallic elements [1–4].

4. Conclusions

Added V_2O_5 not only enlarges the reversible capacity of lithium storage but also enhances the cycling behavior. This is due to the fact that the added V_2O_5 increases the distance between the 002 planes in the carbon and acts as a nucleating agent that causes the carbon to form a layer-like structure. As a result, the electrochemical properties of polymeric carbons are improved.

Acknowledgements

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