

Short communication

Investigation of the effects of V_2O_5 addition on the electrochemical properties of carbon anodes

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Abstract

Through observation of the binding energy spectra of V_{2p} ($S = 3/2$) and C_{1s} , and ESR measurements, we suggest that the nucleation agent formed during heat-treatment of a mixture of V_2O_5 and melamine-formaldehyde resin (polymeric carbon) is the complex $VO(\text{graphene})_2$. First, this complex enables the carbon structure to become more ordered and increases its d_{002} value. Second, the VO displays electron-absorbing ability. Third, the content of the imperfect carbon structure is decreased. All of these effects result in increased capacity and improved cycling behaviour of lithium secondary batteries using such material as the anode. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Lithium secondary batteries, using a lithium transitional element oxide as the cathode, have many advantages over traditional rechargeable batteries and therefore, have attracted the attention of physicists, chemists and materialists in many parts of the world. In commercial designs, the anode is usually graphitic carbon material. The manufacture of this kind of carbon material requires high-temperature processing ($> 2000^\circ\text{C}$) and its reversible capacity for lithium storage is quite limited compared with lithium metal. Thus, many methods are employed to lower the preparation temperature and to increase the reversible capacity.

To date, many kinds of carbons have been investigated [1–5]. They have higher reversible capacities than the theoretical value for graphite, namely, 372 m Ah g^{-1} , and their preparation temperature is lower than 1000°C . On the other hand, their cycling performance is not good. Recently, we reported [6] a method to improve the electrochemical properties of polymeric carbon by adding V_2O_5 to the carbon precursors. The resulting reversible capacity is increased and the cycling properties are improved. The main cause is that the added V_2O_5 can form a nucleation

agent, which results in an increased d_{002} value and a modified carbon structure. The nature of the nucleation agent and its specific effects on discharging and charging are still to be decided.

In this paper, measurements of X-ray photoelectron spectra (XPS) and electron spin resonance (ESR) are employed to reveal the specific effects of V_2O_5 addition and to identify the nucleation agent.

2. Experimental

Polymeric carbons from melamine-formaldehyde resin, with or without the addition of V_2O_5 , were prepared as reported previously [6]. The discharge–charge behaviour of these carbon anodes was obtained by using lithium metal as both the counter and the reference electrode. The electrolyte was a mixture of EC and DEC (volumetric ratio = 3:7) dissolved in 1-M LiClO_4 . The separator was an in house porous polypropylene film.

X-ray photoelectron spectra were obtained with an ES300 instrument from Kratos. The X-ray source was $\text{MgK}\alpha$ and graphite was used to benchmark the position of the binding energy.

ESR measurements were carried out with an EPR200 instrument. The modulation frequency was set at 100 kHz and the microwave power was fixed at the current that

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gave the optimum output effect. Data were obtained at room temperature. As different kinds of radicals or metal compounds have different ESR reactivity, a standard sample was not used to determine the spin concentration.

3. Results and discussion

The discharge curves of carbon anodes, with or without the addition of V_2O_5 prepared at different temperatures are shown in Figs. 1 and 2. V_2O_5 is usually used as a cathode material for lithium secondary batteries, lithium intercalates and de-intercalates at high voltage (> 2.5 V). In this study, the charge curves are almost the same. This means that the added V_2O_5 does not act as a host material for lithium intercalation and its action on the charge curves is negligible. There is, however, an increase in discharge capacity between 0.8 and 0.2 V. This indicates that the addition of V_2O_5 affects the carbon structure.

The $V_{2p}(S = 3/2)$ binding energy spectra of carbons prepared at 600 and 800°C are shown in Fig. 3a,b, respectively. The data reveal a clear change in the V_2O_5 spectra. Part of the V_2O_5 still exists as pentaoxide divanadium, corresponding to a binding energy peak at 516.7 eV, and part exists as vanadium compound of lower valency, corresponding to a binding energy peak at 515.2 eV. The carbon obtained at 800°C has a higher content of low-valency vanadium compound than that obtained at 600°C.

The C_{1s} binding energy spectra of carbon obtained at 600°C and with and without V_2O_5 are shown in Fig. 4a,b, respectively. Clearly, a new kind of carbon atom appears in the presence of 2 wt.% V_2O_5 ; its binding energy is 289.3 eV. Furthermore, three other types of carbon atoms still exist, which are represented by binding energy peaks at 287.4, 286.1 and 284.9 eV, respectively.

The C_{1s} binding energy spectra of carbon prepared by heat-treatment at 800°C, with or without the addition of V_2O_5 are the same as those for the sample prepared at 600°C (cf. Figs. 4 and 5).

When polymer is heated at a temperature below 1000°C, it produces carbon with single, double or triple sheets of

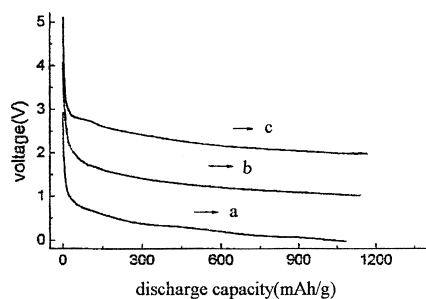


Fig. 1. Discharge curves of carbon anode prepared by heat-treatment at 600°C: (a) without addition of V_2O_5 ; (b) with 1 wt.% V_2O_5 ; (c) with 2 wt.% V_2O_5 . Note, for clarity, the voltage curves of (b) and (c) are shifted by 1.0 and 2.0 V, respectively.

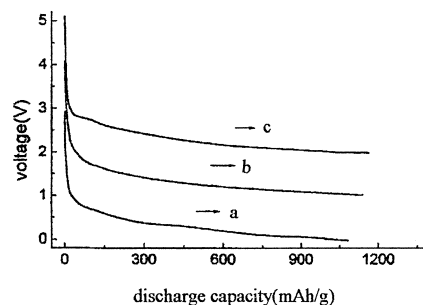


Fig. 2. Discharge curves of carbon anode prepared by heat-treatment at 800°C: (a) without addition of V_2O_5 ; (b) with 1 wt.% V_2O_5 ; (c) with 2 wt.% V_2O_5 . Note, for clarity, the voltage curves of (b) and (c) are shifted by 1.0 and 2.0 V, respectively.

graphene [7]. The graphene molecules are arranged disorderedly in the carbon structure. If one graphene molecule is set, then it will be a formation catalyst or nucleation agent and the stacking of graphene molecules will be less random and, perhaps, more ordered.

It is known that carbon will reduce V_2O_5 when the materials are heated together, and will result in the formation of low-valent vanadium compounds [8,9]. Vanadium carbide can also react with V_2O_5 at temperatures, below 1600°C to form vanadium oxycarbide [10]. Undoubtedly, the heat-treatment of melamine-formaldehyde resin is a carbonization process. Though the resulting carbon is disordered or amorphous and doped with heterogeneous atoms such as N and H, it can also reduce V_2O_5 . This suggestion is consistent with the results in Fig. 3. The $V_{2p}(S = 3/2)$ binding energy of the low-valent vanadium compound is 515.2 eV, i.e., close to that of $VO(acac)_2$. This suggests that the formed compound is not pure low-valent vanadium oxide.

Among the low-valent vanadium oxides, viz., VO_2 , V_2O_3 and VO, only VO can complex with the graphene molecules which are formed during the heat-treatment

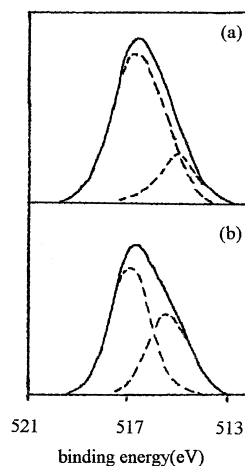


Fig. 3. X-ray photoelectron spectra of $V_{2p}(S = 3/2)$ in carbon after heat-treatment at: (a) 600°C; (b) 800°C.

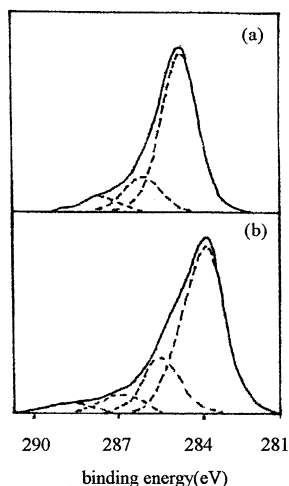


Fig. 4. X-ray photoelectron spectrum of C_{1s} in carbon prepared by heat-treatment at 600°C : (a) without addition of V_2O_5 , (b) added with 2 wt.% V_2O_5 .

process. The vanadium oxycarbide suggested above is perhaps the complex of VO with graphene molecules, i.e., $\text{VO}(\text{graphene})_2$. Its formation is shown schematically in Fig. 6. Vanadium oxide, VO, is very stable after complexing with graphene molecules. Thus, the binding energy peak at 515.2 eV represents the compound of $\text{VO}(\text{graphene})_2$. Its formation is also consistent with the change in C_{1s} binding energy peaks as shown in Figs. 4 and 5. At the same time, a new binding energy peak of C_{1s} appears at 289.3 eV and this indicates that the part of the VO has some electron-absorbing property.

Further information can be obtained from ESR spectra. Fig. 7a,b presents the ESR spectra of the prepared carbons; results are also given in Table 1.

The ESR spectrum of pure carbon (Fig. 7a) consists of a single line without a hyperfine structure. The g factor of pure carbon is 2.0024 and is near to that of a free electron

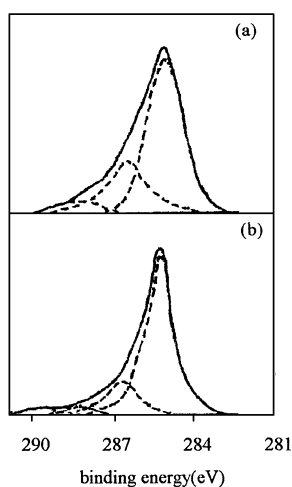


Fig. 5. X-ray photoelectron spectrum of C_{1s} in carbon prepared by heat-treatment at 800°C : (a) without addition of V_2O_5 , (b) added with 2 wt.% V_2O_5 .

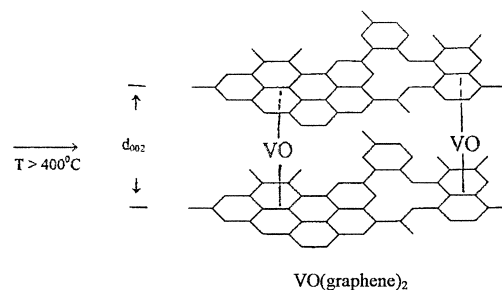
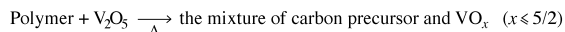


Fig. 6. Schematic of the formation of $\text{VO}(\text{graphene})_2$ prepared by heat-treatment of the mixture of melamine-aldehyde resin and V_2O_5 .

or radical, viz., 2.0023. This suggests that the radical spins in the pure carbon have a π -nature. As shown in Table 1, the value of ΔH for pure carbon is larger than that for usual disordered carbons [11]. Perhaps, it is due to the existence of oxygen atoms in carbon structure [12].

After addition of V_2O_5 , the ESR spectrum (Fig. 7b) consists of two kinds of peaks, termed peak I and peak II. Peak I is near to that of pure carbon, its g factor is 2.0111 and ΔH becomes narrower. Peak II is much broader with a ΔH of 93.21 G and a g factor of 1.9555. It is a typical peak for a transitional metal element compound. Of course, it is not that for V_2O_5 . It could arise from the complex $\text{VO}(\text{graphene})_2$. Since VO is coordinated with graphene molecules, its relaxation time becomes long, and results in overlapping of the spin signals such that its superfine structure is not discernible and takes the form of a broad coupling peak.

From the comparison of peak I with that of pure carbon, it can be concluded that the carbon structure is changed. The relative spin intensities indicate that the content of imperfect structure is much decreased after addition of V_2O_5 . This is because the ESR signal intensity partly reflects the imperfect structure in carbon.

The above discussion indicates that the nucleation agent is the compound $\text{VO}(\text{graphene})_2$ and that it promotes a more ordered carbon structure. Therefore, electron micrographs [6] reveal a layer-like carbon structure of the type observed for graphite. The formation of $\text{VO}(\text{graphene})_2$ appears to result from the intercalation of VO between the

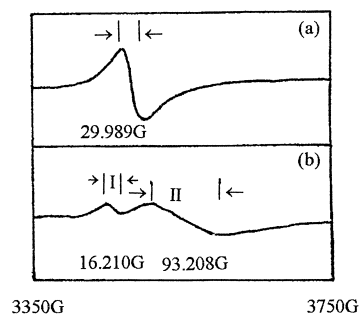


Fig. 7. ESR spectra of carbon prepared at 800°C : (a) pure carbon; (b) carbon doped with 2 wt.% V_2O_5 .

Table 1
ESR data for carbon materials

Sample	<i>g</i> factor	ΔH (G)	Relative spin intensity (/g)
Carbon free of V ₂ O ₅	2.0024	29.99	3.59×10^5
Carbon with addition of V ₂ O ₅	2.0111	16.21	6.1×10^4
	1.9555	93.21	1.7×10^5

graphene sheets. Thus, XRD measurements show that the distance between 002 planes d_{002} is increased [6]. Furthermore, the content of the imperfect carbon structure is much decreased. Due to these effects, the carbons modified with V₂O₅ display superior cycling behaviour. The increased discharge and charge capacity is probably due to the electron-absorbing characteristics of the VO, as mentioned above. This conclusion is supported by the fact that carbon doped with an electron-deficient element such as boron can exhibit a higher reversible capacity [13]. Since only a limited amount of V₂O₅ can be added, the capacity is only marginally increased.

The above investigation reveals that the action of V₂O₅ is different from that of nickel or cobalt oxide, which also catalyzes the formation of a graphitic structure [14], with parallel and curved layer planes.

4. Conclusions

From XPS and ESR measurements, it is suggested that the nucleation agent formed on heating a mixture of V₂O₅ and polymeric carbon is the complex VO(graphene)₂. This complex favours the interaction of graphene molecules and causes the structure of the carbon to become more ordered, therefore, electron micrographs show a layer-like structure.

At the same time, the imperfect carbon structure is decreased. The formation of VO(graphene)₂ suggests the intercalation of VO between graphene molecules, therefore the d_{002} value of the carbon is increased. The VO part of the complex provides an electron-absorbing ability. All these effects result in an increased reversible capacity of lithium storage and enhanced cycling behaviour.

Acknowledgements

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