

RECHARGEABLE LITHIUM BATTERY BASED ON PYROLYTIC CARBON AS A NEGATIVE ELECTRODE

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Summary

We have developed a new type of rechargeable lithium battery composed of a pyrolytic carbon as negative electrode, a metal oxide as positive electrode, and a nonaqueous electrolytic solution. The main feature of this battery is the use of a new pyrolytic carbon, obtained by chemical vapor deposition of hydrocarbon, as a lithium intercalation electrode. The pyrolytic carbon has a layered structure whose interplanar spacing is larger than that of graphite. The size of the crystallites is extremely small. Lithium can be electrochemically intercalated into this carbon electrode in a nonaqueous electrolytic solution such as LiClO_4 in propylene carbonate at room temperature. The electrode shows good reversibility and its coulombic efficiency is greater than 99%. The battery has a long cycle life and endures deep discharge.

Introduction

One of the more fundamental problems that prevent the practical use of rechargeable lithium batteries is the poor cycleability of the lithium negative electrode. The improvement of lithium electrodes and electrolytes has been studied in an effort to overcome this problem. As an alternative to a conventional lithium electrode, we have developed a new type of carbon electrode which electrochemically reversibly reacts with lithium. The electrode consists of carbon obtained by chemical vapor deposition of hydrocarbon. As this electrode works without lithium deposition and forms no lithium dendrites during charge-discharge cycling, a long cycle life is expected. We have constructed a new type of rechargeable lithium battery involving the carbon electrode as negative electrode and metal oxides as positive electrodes. This paper describes the performance of the batteries and the electrode characteristics.

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Experimental

Carbon negative electrode

The electrode consisted of pyrolytic carbon on a substrate prepared by the atmospheric chemical vapor deposition technique. Benzene vapor, supplied by bubbling, and argon carrier gas were fed to a reactor tube, heated at *ca.* 1000 °C, where it flowed over the substrate. Benzene molecules on the substrate decomposed to form graphite-like carbon. Figure 1 shows the apparatus used for the preparation of the pyrolytic carbon. The carbon was removed from the reactor tube and pressed onto a nickel mesh.

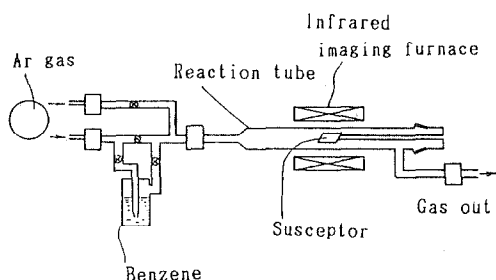


Fig. 1. Apparatus used for the preparation of the pyrolytic carbon.

Metal oxide positive electrodes

The metal oxides used in this study were vanadium oxide and chromium oxide. Vanadium oxide was prepared by heating the NH_4VO_3 aqueous solution at 240 °C. Chromium oxide was prepared by heating a mixture of crystalline Cr_2O_3 and water [1]. Figure 2 shows block diagrams for the preparation of the metal oxides. The preparation of the positive electrodes was as follows: the metal oxide was ground and mixed with Teflon powder as binder and acetylene black as conductor. The mixture was hot-pressed onto a stainless steel mesh and was dried under vacuum.

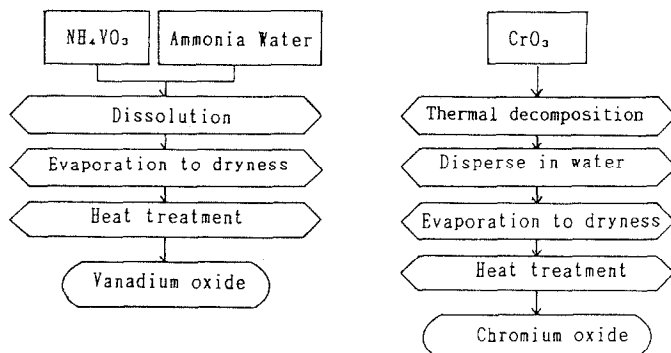


Fig. 2. Block diagrams for the preparation of the metal oxides.

Cell construction

The positive and negative electrodes were separately charged and discharged with lithium counter and reference electrodes in 1 M LiClO_4 -propylene carbonate electrolyte. The electrodes were then assembled into a cell. The electrolyte in the cell was 1 M LiClO_4 dissolved in propylene carbonate. Two types of cell construction were used: coin shaped and thin-film shaped.

Results and discussion

A great deal of research involving cathodic intercalation into graphitic carbons in organic electrolyte solutions has been reported [2 - 4]. In the case of lithium intercalation into graphitic carbon from LiClO_4 /propylene carbonate electrolyte, it has been reported that the decomposition of propylene carbonate and the formation of lithium graphite intercalation compounds occurred simultaneously at the graphite cathode yielding propene [5 - 7]. In our study we found a new type of graphitic carbon into which lithium can be intercalated without decomposition of the propylene carbonate.

Figure 3 shows the X-ray diffraction pattern of this pyrolytic carbon. The Bragg peak of the (002) plane was broader than the graphite peak, and the calculated interplanar spacing of the carbon was larger than that of graphite. The (110) peak was not observed. These results suggest that the pyrolytic carbon has a layered structure whose distance between layers is larger than that of graphite and the crystallite size is extremely small. The mean interplanar spacing was *ca.* 0.349 nm, calculated from the X-ray diffraction pattern. The size of the crystallite in the *C*-axis direction, determined from the half-width value of the diffraction peak, was below 10.0 nm.

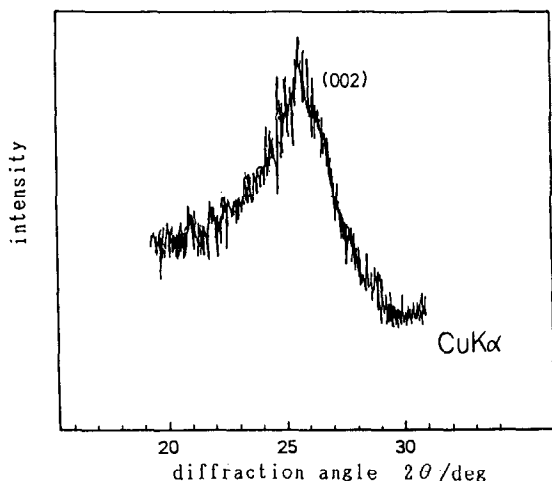


Fig. 3. X-ray diffraction pattern of the pyrolytic carbon.

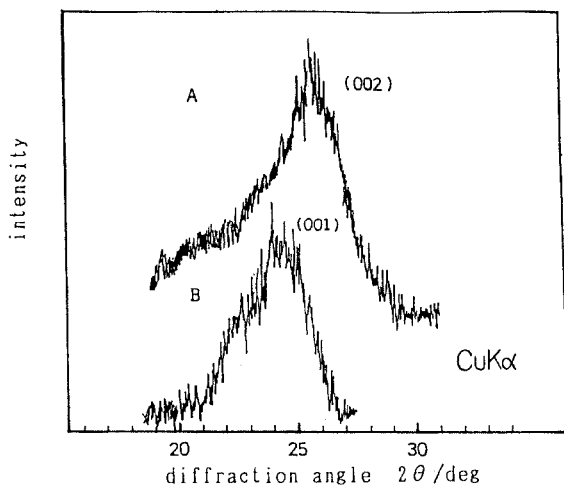


Fig. 4. X-ray diffraction patterns of the carbon electrode before (A) and after (B) lithium insertion.

Figure 4 shows the X-ray diffraction patterns of this carbon electrode before (A), and after (B), lithium insertion. After lithium insertion, the (002) peak vanished and a peak shifted to a lower angle was observed. The interplanar spacing calculated from the low angle shifted peak was 0.371 nm. The value agreed with that of Li-GIC(C_6Li) [8]. This result suggests that lithium was intercalated into the carbon electrode and formed an intercalation compound.

Figure 5 shows the electrical potential changes of the carbon electrode during charge/discharge tests. During charge/discharge cycles between 0 V and 2.5 V *versus* Li/Li^+ , neither lithium deposition on the electrode nor any degradation of the electrode was observed. The coulombic efficiency was above 99%.

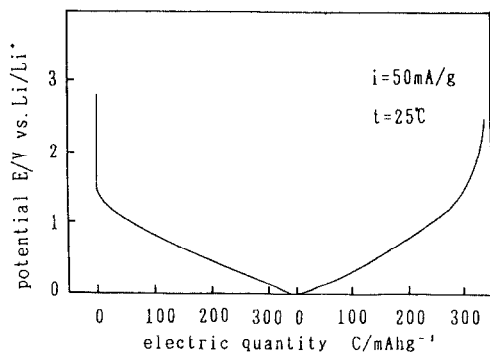


Fig. 5. Changes in electric potential of the carbon electrode during charge/discharge tests.

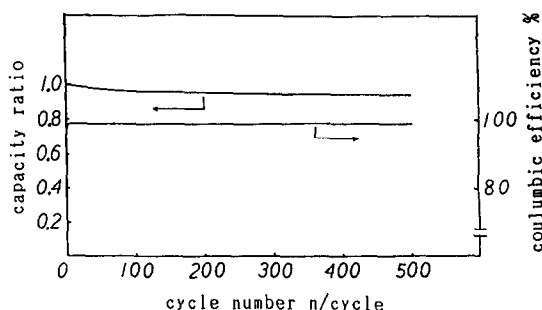


Fig. 6. Capacity and coulombic efficiency dependencies of the carbon electrode on cycle number.

Figure 6 shows the capacity and the coulombic efficiency dependencies of the carbon electrode on cycle number. These results suggest that decomposition of the electrolyte solution and an irreversible reaction does not occur when using the pyrolytic carbon as a negative electrode. The pyrolytic carbon is a graphitic carbon with a wider interplanar spacing than that of graphite, and the size of the crystallites is extremely small compared with that of graphite. It is our understanding that this is the reason for the formation of the lithium graphite intercalated compound without decomposition of the propylene carbonate.

Chromium oxide and vanadium oxide were chosen as positive electrodes in this study. No sharp peaks were observed in the diffraction pattern of Cr_2O_3 . The result was in good agreement with previously reported results [9]. The chromium-oxygen stoichiometry was about 1:2.55, which was determined by TGA.

X-ray diffraction patterns of vanadium oxide were different from that of the crystalline vanadium oxide, but were similar to the patterns of V_2O_5 -gel [10]. The water contained in the vanadium oxide was determined using TGA in air. From the result, the composition of this sample was determined at $\text{V}_2\text{O}_5 \cdot 0.53\text{H}_2\text{O}$. These compounds have good cycleability, and are capable of intercalation over a limited composition range. If a positive electrode made from these compounds is combined with a negative electrode of large capacity such as Li metal or Li-Al alloy, deep cell discharge causes excessive intercalation. Therefore, to avoid degradation, the cell must not be discharged to low voltage. This is one of the most serious problems in the application of the rechargeable lithium battery. Because the pyrolytic carbon is stable as a negative electrode and contains a limited amount of lithium, the positive electrode can be prevented from excess lithium intercalation and the cell endures deep discharge. Figure 7 compares the discharge curves of the cell before, and after, discharge to 0 V. Figure 8 displays charge/discharge curves of the pyrolytic carbon/vanadium oxide coin-shape cell. Figure 9 illustrates the charge/discharge curves of the pyrolytic carbon/chromium oxide thin-film-shape cell. These cells had a long cycle life.

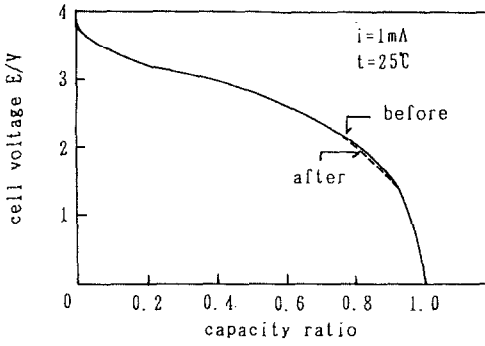


Fig. 7. Discharge curves of the cell before, and after, discharge to 0 V.

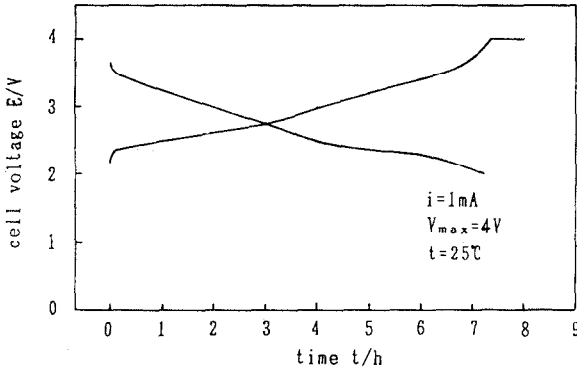


Fig. 8. Charge/discharge curves of the pyrolytic carbon/vanadium oxide coin-shape cell.

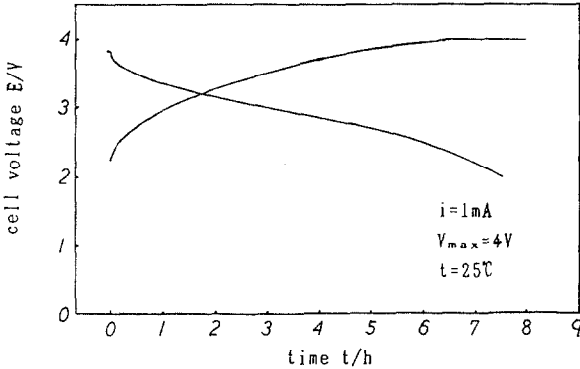


Fig. 9. Charge/discharge curves of the pyrolytic carbon/chromium oxide thin-film-shape cell.

Figure 10 shows the capacity *versus* cycle number for the pyrolytic carbon/chromium oxide thin-film-shape lithium battery which, despite an internal pressure rise, had a life of more than 500 cycles.

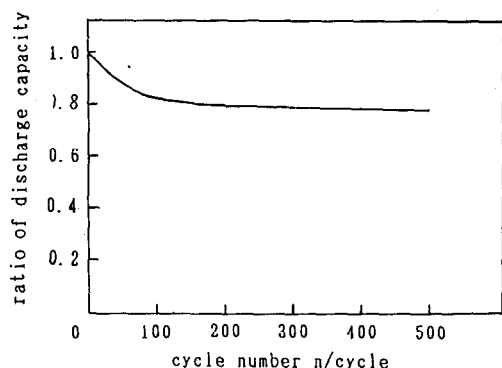


Fig. 10. Capacity vs. cycle number for the pyrolytic carbon/chromium oxide thin-film-shape cell.

Conclusion

The pyrolytic carbon electrode has good reversibility over a wide range of electric potential. It is free from lithium dendrite formation and is an excellent negative electrode for a rechargeable lithium battery. Using the carbon and metal oxide electrodes, it is possible to produce rechargeable lithium batteries.

References

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