

Anodic behavior of a carbon plate in an LiCl–KCl binary molten salt

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Accepted 10 December 1996

Abstract

The behavior of a negative pole of a carbon plate (a mixture of graphite with glassy carbon) in a eutectic LiCl–KCl binary molten salt has been investigated at 360–500 °C. as a fundamental study on high temperature lithium secondary cells. Both cyclic voltammetric and galvanostatic charge/discharge data suggested that reversible insertion/extraction of lithium can take place accompanied by stage formation. The interlamellar distance of carbon increased upon lithium insertion and the coulombic efficiency became higher with galvanostatic cycle number. © 1997 Published by Elsevier Science S.A.

Keywords: Carbon anodes; Lithium secondary cells; Molten salt

1. Introduction

Recently, lithium secondary cells having a high voltage and high energy density are attracting much attention. The so-called intercalation- or insertion-type electrode is used as a cathode and/or an anode in these cells, and hence their dynamic features tend to be controlled by the mass transport processes in the solid phase of the active material. In other words, better dynamic performance might be expected for these lithium cells at a higher temperature due to the accelerated mass transport.

As for high-temperature lithium secondary cells, several attempts have so far been made [1–7]. However, only the Li–Al alloy/FeS₂ cell at 450 °C [1] seems to be practically applicable at present in spite of a problem that the volume of an Li–Al alloy changes considerably during cycling.

In a previous work [8], we investigated the electrochemical insertion/extraction of lithium into/from carbon (a natural graphite–glassy carbon mixture) plate from/into the LiCl–KCl binary molten salt electrolyte and showed that the insertion/extraction processes can take place reversibly to some extent and that the formed Li–C compound is unstable at least above 400 °C. In the present study, the experimental temperature was set at 352 °C just above the eutectic temperature) of the 59mol%LiCl–41mol%KCl binary melt in order to suppress the decomposition of lithiated carbon.

2. Experimental

Fig. 1 shows the electrochemical cell configuration. A eutectic LiCl–KCl binary molten salt (LiCl: 59 mol%, KCl: 41 mol%, m.p. 352 °C) was used as the electrolyte. Impurity water in this melt was removed by bubbling argon gas at 500

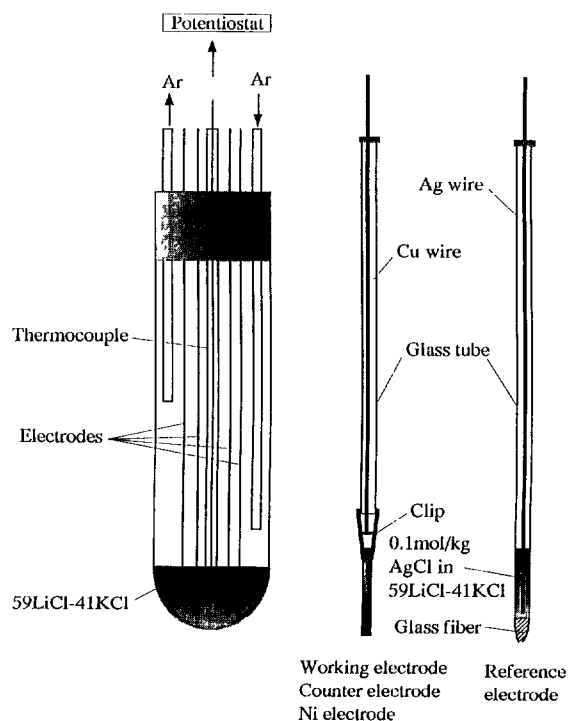


Fig. 1. Schematic illustration of the experimental cell and electrodes

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°C for over 10 h. A densely molded carbon plate (a graphite-glassy carbon mixture of 0.8 mm in thickness, prepared originally for fuel cells) was chosen as the main sample. The counter electrode was a pyrolytic carbon plate or an Li–Al alloy. The reference electrode was an Ag/Ag⁺ (0.1 mol/kg AgCl in 59LiCl–41KCl) electrode and its potential was proofread by a nickel electrode on which lithium was freshly deposited. All electrochemical measurements were carried out blowing argon gas above the melt in a Pyrex cell. X-ray diffraction (XRD) measurements of the carbon plates were performed both before and after charging down to the reversible Li/Li⁺ potential (–2.58 V versus Ag/Ag⁺ electrode) in the melt at 400 °C to investigate the structural changes due to lithium insertion.

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 2 shows typical cyclic voltammetric (CV) curves of a carbon electrode at 0.6 mV/s. Several current peaks appearing on both the cathodic and the anodic sides ensure clearly that insertion/extraction of lithium occurs reversibly to some extent accompanied with the step-wise stage formation of the Li–C compound as well as in many studies of carbon materials in non-aqueous solutions at room temperature [9]. The magnitude of all these peak currents tends to decrease with cycle number and the electrochemical processes seem to become difficult to occur gradually.

3.2. XRD data after lithium insertion

After galvanostatic charging at 40 mA (~200 mA/cm²) down to the Li/Li⁺ potential, the carbon electrode was taken

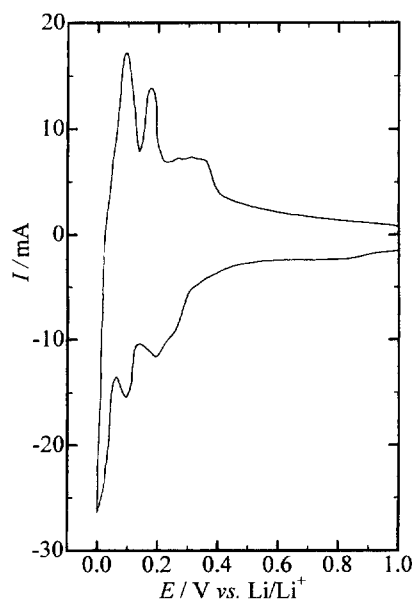


Fig. 2 Typical CV curves at ±0.6 mV/s; third cycle, 400 °C

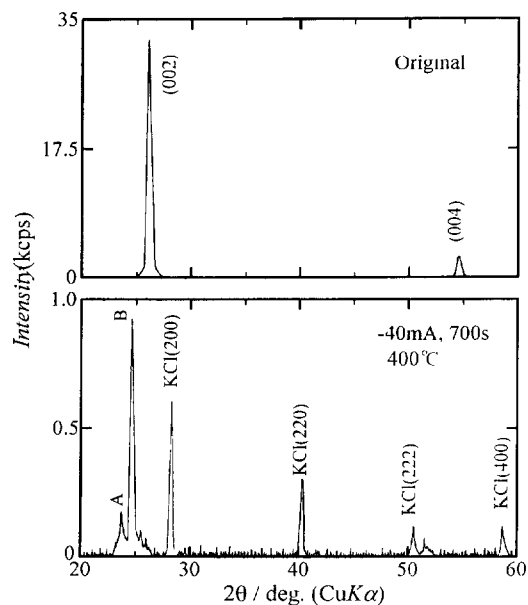


Fig. 3. XRD patterns of a carbon plate before and after galvanostatic cycling.

out of the electrolyte and the solidified melt adherent to the carbon surface was removed with emery papers. Then the carbon plate was set on an XRD sample holder. All of these procedures were done in an argon-filled glove box. Fig. 3 shows the XRD patterns of this sample comparing with those of an original sample. As seen in this figure, the (002) diffraction peak of an original sample at $2\theta = 26^\circ$ (corresponding to the interlayer spacing of 0.340 nm) was split into two peaks A and B at $2\theta = 23^\circ$ – 24° after suffering from electrochemical lithiation. The observed peak splitting suggests that two kinds of Li–C compound are formed probably. We can assume that ‘peak A’ and ‘peak B’ correspond to the formation of the first stage and the second stage, respectively, referring to the reported interlamellar expansion of carbon due to electrochemical lithiation from a non-aqueous electrolyte solution [10]. Then, in case of a lithiated sample of Li_{0.31}C₆ (on the coulombic basis, cf. Fig. 3), the spacing of lithium-accommodated layer can be calculated as 0.379 nm for the stage-1 structure and as a nearly equal value of 0.382 nm for the stage-2 structure. Thus, the interlayer expansion of carbon due to lithium insertion in this case amounts to ~0.04 nm.

From these results, we may conclude that lithium insertion to this sample carbon plate can take place electrochemically in this melt.

3.3. Charge and discharge curves

Fig. 4 shows typical galvanostatic charge/discharge curves. Several potential plateaus above 0 V show that electrochemical insertion/extraction of lithium into/from a carbon plate occur reversibly to some extent. As can be seen in Fig. 5, both the charge capacity and the discharge capacity decrease with repeating the galvanostatic cycles between 0 V (Li metal deposition) and 3.5 V (Cl₂ evolution), although

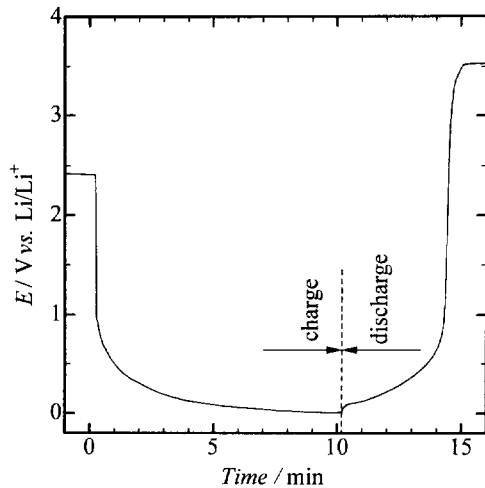


Fig. 4. First charge/discharge curves at ± 40 mA and 400°C .

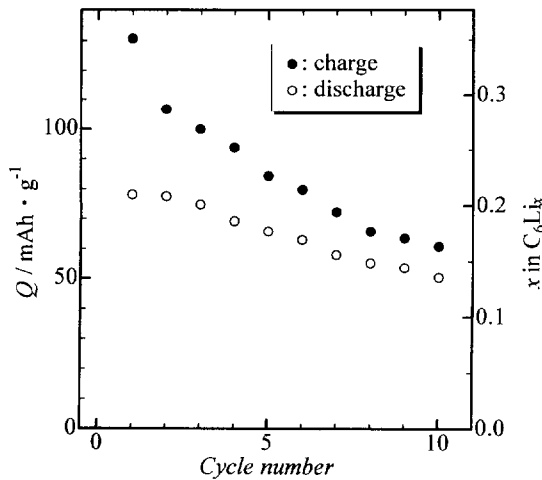


Fig. 5. Changes in charge and discharge capacities with repeating cycles at ± 40 mA; 0–3.5 V, 400°C .

the discharge/charge coulombic efficiency increases from 60 to 85% after ~ 10 cycles.

3.4. Stability of the Li–C compound in the eutectic LiCl–KCl melt

At least above 400°C , the cathodically formed Li–C compound seems unstable and having suffered from the decomposition in the electrolyte used. The decrease in discharge capacity with increasing open-circuit (OC) pause is shown in Fig. 6, where OC immersion periods were set between charge and discharge operations. This phenomenon is confirmed to be more remarkable with a higher cell temperature.

Furthermore, the OC potential after charging does not stay near 0 V but increases to above 1.0 V, as illustrated in Fig. 7. From these results the following two reasons might be considered why the coulombic efficiency for the charge/discharge cycling does not reach at 100% in the present case.

Firstly, the Li–C compound decomposes thermally at a high temperature as suggested from the fact that the discharge capacity decreases more rapidly at a higher temperature

(Fig. 6). However, the occurrence of lithium metal is not yet confirmed analytically in the electrolyte at present.

The second reason may be the mechanical destruction of a carbon plate caused by the expansion/shrinkage of the *c*-axis of graphite during charge/discharge cycling with intercalation/de-intercalation of lithium. Actually, the roughening of the carbon electrode surface after the electrochemical cycles can be observed by scanning electron microscopy (SEM).

Based on the equilibrium phase diagram of the Li–C system [11] (Fig. 8), the formed compound (apparent average formulae of $\text{Li}_{0.31}\text{C}_6$ on the coulombic basis) should belong to 'stage-1 gas' formed at above 400°C , where 'stage-1 gas' denotes the phase that lithium exists in all interlamellar gaps at a lower density than in the normal stage structure of 'stage-1 liquid'. At a high temperature as used in this work, the high stage structures of the Li–C compound should be unstable, since thermal perturbation of guest lithium atoms exceeds the coulombic intralayer interaction. Nevertheless, several cur-

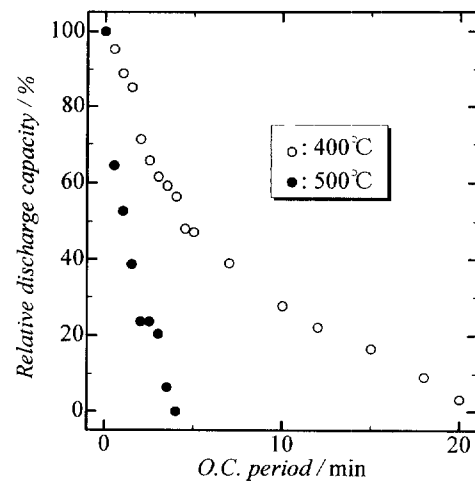


Fig. 6. Decrease in discharge capacities with the length of the OC pause between charge and discharge operations at ± 40 mA, 0–3.5 V.

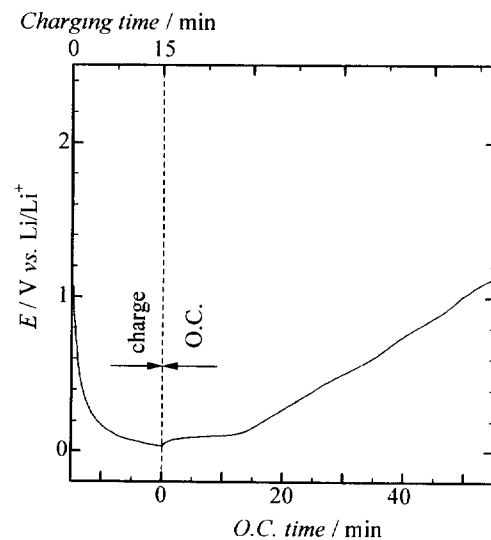


Fig. 7. Gradual shift of OC immersion potential after charging at ± 40 mA, 400°C .

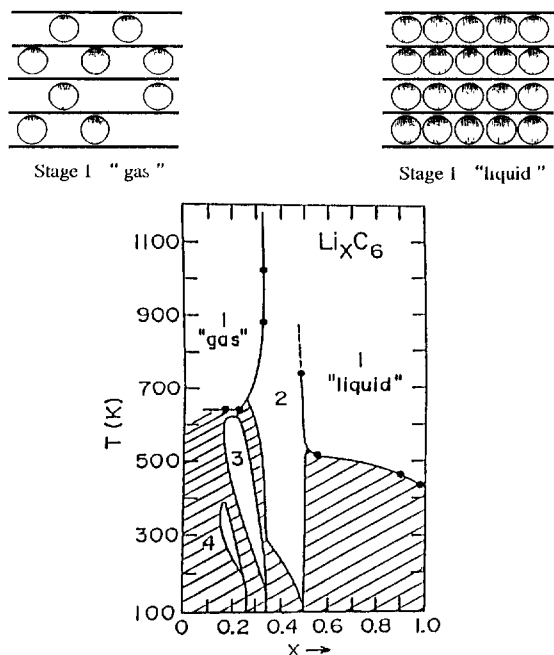


Fig. 8. Staging phase diagram for Li_xC_6 derived from X-ray and neutron diffraction experiments [11].

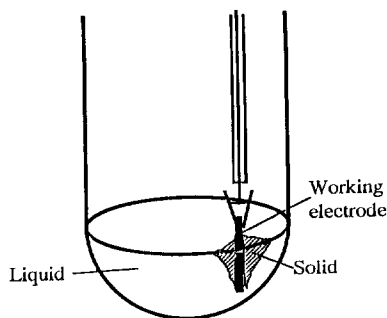


Fig. 9. Schematic setup of the local solidification of the electrolyte near the carbon surface at 360 °C.

rent peaks, characteristic of the stepwise staging, are in fact observed as in Fig. 8. This fact suggests that the non-equilibrium phenomena are concerned with the present electrochemical processes. The gradual shift of OC potentials after charging (Fig. 7) may also be related to the relaxation from non-equilibrium states of high stage structures in the graphite layers.

When we lower the experimental temperature to 360 °C slightly above the eutectic point, both the charge and the discharge capacities become greater than those at 400 °C for several initial cycles. Since the discharge capacity is always smaller than the charge capacity, however, the shortage of Li^+ ions in the melt occurs at the carbon surface. As a consequence, the crystallization of KCl occurs at the carbon surface, as illustrated in Fig. 9, and the further electrochemical processes become difficult to be continued after ~10 cycles.

4. Conclusions

Electrochemical insertion/extraction of lithium to/from a thin carbon plate (a mixture of graphite and glassy carbon) from/to a eutectic LiCl-KCl binary melt can proceed reversibly to some extent. Especially, several current peaks characteristic of the stepwise staging can be observed by cyclic voltammetry. However, the cathodically formed Li-C compound is unstable at a high temperature and its decomposition seems inevitable. It is necessary in further studies to operate the cell at a lower temperature by using other electrolytes.

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