



Electrochemical behavior of an advanced graphite whisker anodic electrode for lithium-ion rechargeable batteries

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Abstract

Graphite whiskers, produced by Nikkiso Co., Ltd., (sample code 2GWH-2A) have been investigated with respect to their electrochemical characteristics in different types of liquid electrolytes: LiClO₄, LiPF₆, LiAsF₆, LiBF₄, LiCF₃SO₃ in ethylene carbonate–diethyl carbonate and in solid electrolytes. A high capacity (363 mAh/g) is obtained when a liquid electrolyte was used and 330 mAh/g at 80 °C in the case of a polymer electrolyte. The coulombic efficiency during the first cycle is lower when polymer electrolyte is used. 2GWH-2A shows very different performances in LiClO₄ and in LiPF₆ electrolytes. The degree of intercalation depends upon of the nature of the binder, composition of the electrode and electrolyte. The color of the carbon electrode also changed from black to gold in the presence of some lithium salt electrolytes, when lithium was fully intercalated into the electrode. The galvanostatic charge/discharge tests show a large plateau near 0 V. On measuring the slow cyclic voltammogram of the 2GWH-2A, five cathodic peaks were observed.

Keywords: Graphite whisker; Lithium-ion batteries; Anodes; Carbon–lithium; Polymer electrolytes

1. Introduction

In the past decade there has been much interest in carbon–lithium electrodes to replace metallic lithium in rechargeable batteries because of the adverse effects of the contact between lithium and the electrolyte. The lithium–carbon electrode (with no dendrites) is safer for the lithium rechargeable battery and has a lower working voltage between 0 and 250 mV [1] and high cycleability. This is the new generation of secondary batteries, the so-called ‘rocking-chair’ [2] or lithium-ion systems [3] in which, contrary to primary batteries, the lithium is in the ionic state in the anode and cathode, and also in the electrolyte. In general, graphite has a theoretical capacity of 1 Li per C₆: this corresponds to a specific capacity of 372 mAh/g. Lithium was cathodically intercalated into the graphite whisker from liquid or solid electrolyte, in which some charge is irreversibly consumed in the formation of an Li⁺-conducting passivation film. Subsequent to the first

cycle, the cell exhibited excellent reversibility, which depends also on the origin of the carbon and electrolyte [4]. It shown for the first time, that the reversible capacity depends on the preparation method and on the diameter of the vapor-grown carbon fiber [5]. In addition, we aim to study a large variety of electrode forms (tissues, pellets, paints) that can be formed using graphite whiskers without any addition of electronic conductor, e.g., acetylene black or carbon black. We elsewhere investigated 20 types of graphite whiskers to demonstrate the relationship between the change of color and the electrochemical behavior with a large variety of liquid and solid electrolytes, because the high cycleability depends strongly on the nature of the electrolyte and the binder [1].

This report is focused on the whisker that demonstrated the highest reversible capacity and we have considered the effects of the nature of the electrolyte and binder on the performance of the lithium–carbon electrode. We will discuss these results concerning the graphite whisker electrode being in contact with the liquid and polymer electrolyte.

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2. Experimental

2.1. Carbon material

A graphite whisker 2GWH-2A (diameter 2 μm , length 10 μm), was heat-treated at 2800 $^{\circ}\text{C}$ and chopped by procedure 2A [5] (chopping process after graphitization). X-ray diffraction analysis showed a high crystallinity of the carbon whisker. The interplanar spacing d_{002} was 0.3359 nm and the size of crystallite along c -axis (L_c) was 76.1 nm.

2.1.1. Electrode preparation and electrochemical cells

2.1.1.1. Liquid electrolyte

Three types of poly(vinylidene fluoride) (PVDF) were used: KF-1000, KF-1100, KF-1300 (Kureha Chemical Co.) and poly(ethylene oxide) (PEO-NEW, mol. wt. 5.5 million from Sumitomo Seika Co.) were used as binders, and N -methylpyrrolidone and acetonitrile were used as solvent. Two kinds of experimental cells were used:

(i) A three-electrode cell. The working electrode was paint deposited on the nickel mesh and the reference and counter electrodes were lithium sheets.

(ii) A coin-type cell (2430). The coin electrode (diameter = 10 mm) was pressed on to a pellet under a pressure of about 20 kg/cm^2 . The working electrodes were dried under vacuum at 120 $^{\circ}\text{C}$ for 24 h, then set up into the cells without any air contact. Various types of liquid electrolytes (Mitsubishi Petrochemical Co., Ltd.), were used 1 M (LiPF_6 , LiClO_4 , LiCF_3SO_3 , LiBF_4 , LiAsF_6) in ethylene carbonate (EC)–diethyl carbonate (DEC).

2.1.1.2. Solid electrolyte

The polymer electrolyte (Dai-Ichi Kogyo Seiyaku Co., Ltd.), was prepared with PEO and LiClO_4 to give a viscous liquid. UV irradiation with a photo-initiator was used to cross link the material and the polymer was then dried under vacuum at 80 $^{\circ}\text{C}$ for 72 h. The composite electrode was obtained from a mixture containing 70 wt.% whisker and 30 wt.% polymer in acetonitrile. This mixture was deposited on a stainless-steel disc of 15 mm diameter, treated at 65 $^{\circ}\text{C}$ under vacuum to evaporate the acetonitrile. Then it was set up in a button cell.

The apparatus used to measure the electrochemical and physicochemical properties have been described in Ref. [1]. In order to measure the galvanostatic charge/discharge (the current density = 25 mA/g ($C/15$) and the cutoff voltages between 0 and 2.5 V versus Li^+/Li), slow cyclic voltammetry and impedance spectroscopy methods were used. All measurements were carried out at ambient temperature in the case of the liquid electrolyte and 80 $^{\circ}\text{C}$ for the polymer electrolyte.

3. Results

3.1. Liquid electrolyte

Fig. 1 exhibits the first to the fourth charge cycles for 2GWH-2A/Li, using electrolyte 1 M LiPF_6 and four different binders with various proportion ratios. The data listed in this Figure indicate that the four electrodes have high capacities. In order to test if these high capacities were a consistent feature of the electrode composition, further measurements were performed on electrodes using a different electrolyte salt (LiClO_4). The data were gathered using 1 M LiClO_4 and demonstrate that in the case of 2GWH-2A (90%) with KF-1000 (10%) the highest capacity has been obtained. Fig. 2 shows the first to the fourth charge cycles for 2GWH-2A/Li using different liquid electrolytes in ethylene carbonate–diethyl carbonate. These data show that in the case of 1 M LiClO_4 , the first charge (363 mAh/g) is reproducible and not modified by subsequent charge/discharge cycling. The capacity decreases in order of $\text{LiClO}_4 < \text{LiCF}_3\text{SO}_3 < \text{LiAsF}_6 < \text{LiPF}_6 < \text{LiBF}_4$: with exception of LiPF_6 , the color of the carbon electrode also changed from black to gold when lithium was fully intercalated into the electrode.

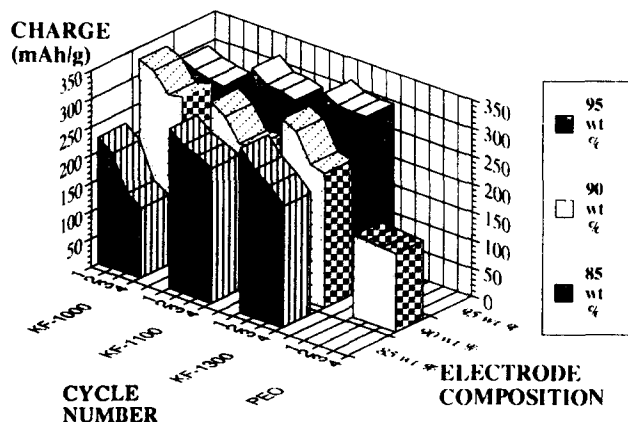


Fig. 1. Effect of poly(vinylidene fluoride) (KF-1000, 1100 and 1300) and poly(ethylene oxide) binders in various proportion ratios in the charge capacity with 1 M LiPF_6 /EC–DEC during the first to fourth cycles.

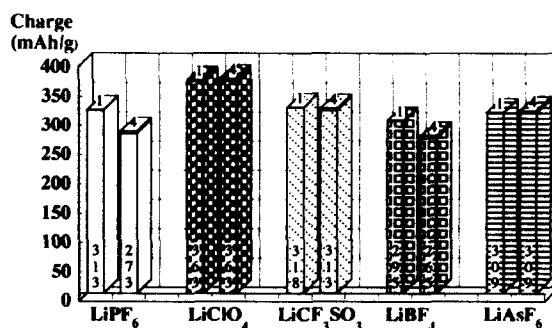


Fig. 2. Electrolyte salts vs. charge capacity of 2GWH-2A (90%) with KF-1000 (10%) during the first and fourth cycles.

Slow cyclic voltammograms of 2GWH-2A (Fig. 3) showed five reduction peaks at respectively 57, 95, 125, 145 and 198 mV whereas in the case of LiPF_6 , only one large peak was observed. X-ray diffraction (XRD) studies (Fig. 4) show that in the case of LiClO_4 only the first stage of intercalation was observed, and in the case of LiPF_6 only the second stage. The state of lithium in 2GWH-2A (Fig. 5) after the first discharge was investigated by nuclear magnetic resonance (NMR). In $\text{LiClO}_4/\text{EC-DEC}$ there is one peak with a Knight-shift of 45 ppm (LiC_6). In the case of 2GWH-2A in $\text{LiClO}_4/\text{EC-DEC}$, the NMR results are favorably comparable with the XRD of the first stage Li-graphite intercalation compounds (gold color).

3.2. Solid electrolyte

The coulombic efficiency of the first cycle (72%) is lower than that using a liquid electrolyte (Fig. 6). This

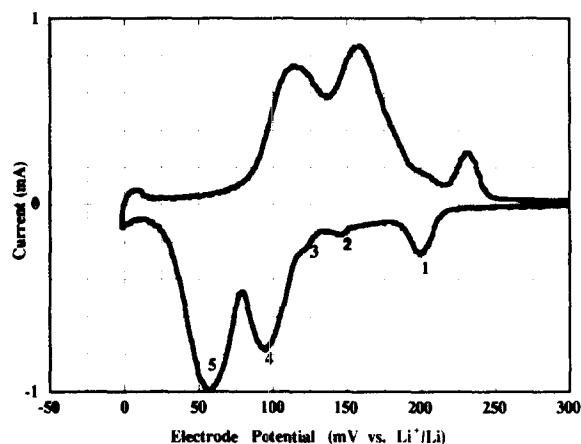


Fig. 3. Voltammogram (15 mV/h) of the second reduction/oxidation cycle of Li/1 M $\text{LiClO}_4/\text{EC-DEC}/2\text{GWH-2A}$ (90%) with KF-1000 (10%).

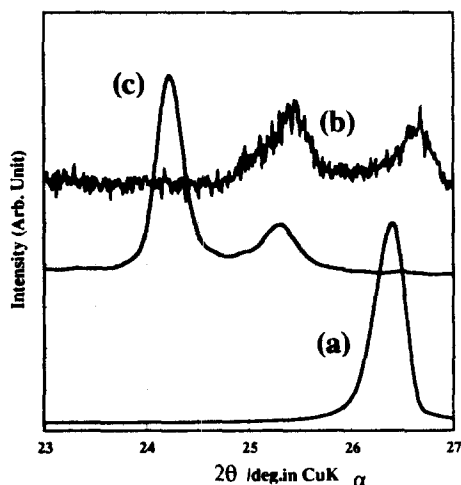


Fig. 4. X-ray diffraction patterns of 2GWH-2A electrode after the first discharge (first lithiation) (a) without treatment; (b) 1 M $\text{LiClO}_4/\text{EC-DEC}$, and (c) 1 M $\text{LiPF}_6/\text{EC-DEC}$.

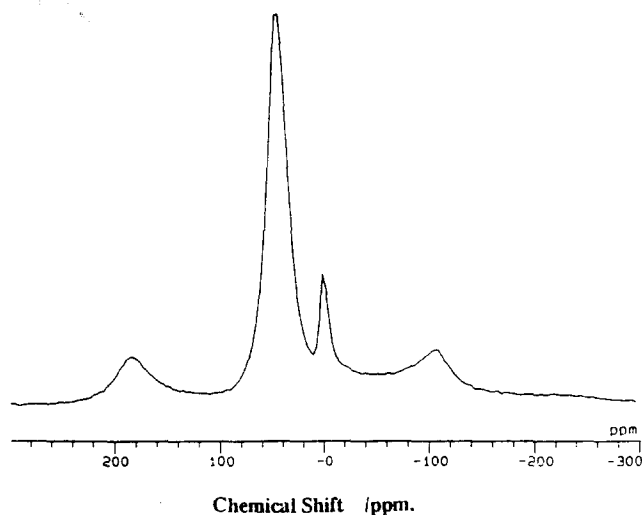


Fig. 5. ^7Li NMR spectra of carbon whisker after the first lithiation (discharge) to 0 V using 1 M $\text{LiClO}_4/\text{EC-DEC}$.

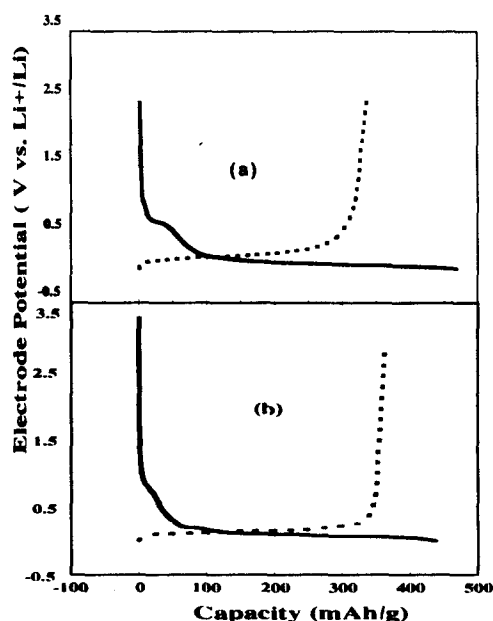


Fig. 6. Comparison of the first cycle discharge/charge voltage curve of an Li/electrolyte/2GWH-2A (—) (discharge = intercalation), and (---) line (charge = deintercalation): (a) with polymer at 80 °C, and (b) electrode with 1 M $\text{LiClO}_4/\text{EC-DEC}$ at 25 °C.

Figure shows that the open-circuit voltage (OCV) of 2GWH-2A was about 3.2 and about 2.5 V, respectively, for the liquid and polymer electrolyte. After the potential has been decreased to 0.8 V, a shoulder was seen in the case of the liquid electrolyte, this irreversible shoulder corresponds to a passivation layer [6], however, for the same range of potential the curve of solid polymer shows a plateau. This irreversible plateau probably also corresponds to the formation of a passivation film. This plateau has not previously been noticed in the case of polymer electrolytes. The galvanostatic charge/discharge shows a large plateau near 0 V. The reversible capacity

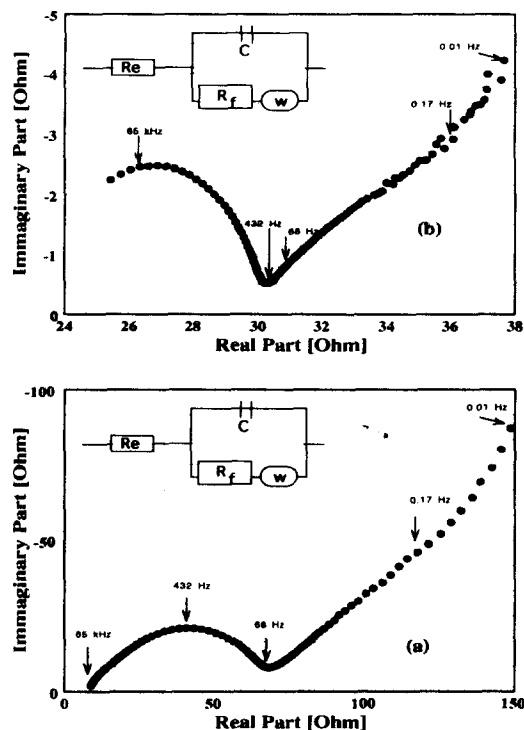


Fig. 7. Impedance spectra for Li/electrode/2GWH-2A cells (a) with polymer at 80 °C, and (b) electrode with 1 M LiClO₄/EC-DEC at 25 °C.

is 330 mAh/g with a coulombic efficiency of 100% at 80 °C, possibly the highest capacity obtained with this solid polymer-type electrode. The existence of the irreversible capacity in both liquid and solid electrolytes may be mainly due to the chemical and electronic state of the surface at the carbon electrode. The impedance behavior Li/electrolyte/2GWH-2A in Fig. 7 is usually approximated by a simple equivalent circuit where W is used to denote the Warburg component for diffusion. These plots were obtained at OCV for virgin cells. The resistance of the liquid electrolyte is 8.90 Ω , however, the resistance of the polymer at 80 °C is 23 Ω , much lower than the value of 1350 Ω at 25 °C. The interfacial resistance using the liquid electrolyte is $R_i = 31.6 \Omega$, in the case of the solid electrolyte it is 3.6 Ω . This difference may be due to the difference in thickness of the passivation layer, the nature of electrolyte and working temperature. The diffusion (penetration) coefficient of lithium using LiClO₄/EC-DEC at 25 °C is $D_1 = 9 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ the value of diffusion coefficient using solid polymer at 80 °C is $D_2 = 7.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. The ratio $R = D_2/D_1 = 8.3$ is due to the nature of the electrolyte and the differences in temperature.

4. Discussion

The irreversible capacity of the first cycle is due, in part, to the formation of a passivation film but may

also be affected by several other factors, including the origin of the carbon, the chemical and electronic surface state of carbon, and the carbon/electrolyte interfacial phenomena. It is speculated that the difference in reversible capacity between the solid and liquid electrolytes may arise from a better wetting of the carbon whisker achieved with the liquid electrolyte when compared with the solid electrolyte. The significance of the binder used in these electrodes is demonstrated by comparing the galvanostatic properties of the samples with varying amounts of 2GWH-2A [6]. Binders are needed to prevent an electrode fracture and to increase the contact between the graphite whiskers within the electrodes. In addition, we cannot neglect the reaction between the solvent and the electrolyte and the nature of the binder, because this reaction is responsible for the cycleability of the Li_xC₆ electrode. It is further speculated that the difference in behavior of the electrodes in LiClO₄ and in LiPF₆ may be due at least in part to chemical (H₂O, etc.) and no electrochemical phenomena.

5. Conclusions

The 2GWH-2A has a high stable reversible capacity 363 and 330 mAh/g, respectively, (with liquid and solid electrolytes), and a high coulombic efficiency ($\approx 100\%$). 2GWH-2A has interesting electrochemical and mechanical properties. The degree of intercalation depends on the nature of the binder, composition of electrode and lithium salts. In both the liquid and polymer electrolytes, the highest capacity is found when LiClO₄ was used. The irreversible capacity is not directly related to the nature of the electrolyte but to the surface of the carbon electrode [7].

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