

Performance of lithium-ion rechargeable batteries: graphite whisker/electrolyte/LiCoO₂ rocking-chair system

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Abstract

A lithium-ion rechargeable battery based on carbon anode, a viable replacement for lithium metal anode, has been developed. Lithium-ion rechargeable batteries are considered to have high capacity and high safety. For this reason, we have investigated rechargeable batteries with higher energy density, and studied host carbon materials for the anode, in particular. In this investigation, the vapour-grown carbon fibre was used as the anode material. This carbon fibre after graphitization showed high capacity (363 mAh/g carbon) and low potential (versus Li/Li⁺). It showed good stability during cycling, and is expected to be a suitable anode material in lithium-ion rechargeable batteries. Further, a coin-type cell was prepared with this carbon anode and LiCoO₂ cathode, and the performance during galvanostatic charge/discharge cycling observed. This coin-type battery has a high energy density.

Keywords: Rechargeable lithium batteries; Carbon anodes; Graphite whisker

1. Introduction

A new generation of high energy, lithium-ion rechargeable batteries have attracted a great deal of attention. Recently, some carbon materials have been investigated as the anode of these batteries by virtue of their high safety, capacity and good stability during cycling. Until now, it has been reported that crystallinity, form and texture of carbon materials is related to its performance when used as the anode in lithium-ion rechargeable batteries. Crystallinity of carbon materials gives differences in the charge/discharge profile and capacity when used as the anode. The low-graphitized carbon anodes show high capacity (about 400 mAh/g) and high potential between 0 and 1.2 V (versus Li/Li⁺) [1–3]. On the other hand, well-graphitized carbon anodes give also high capacity. Further, as these carbon electrodes show low potential near 0 V (versus Li/Li⁺), it is expected that batteries with well-graphitized carbon anodes show high energy density. With regard to the texture of carbon, onion texture is better than the radial one, because the carbon electrode with radial texture was broken at each charge/discharge cycle [4].

The vapour-grown carbon fibre (Grasker[®], Nikkiso Co.) is a soft carbon material and its crystallinity after graphitization is close to that of single crystal graphite,

the latter can be called ‘graphite whisker’. Further, the diameter, length and aspect ratio of this carbon can be changed by controlling the production process. Although it seems difficult to develop a carbon fibre with apparent bulk density or packing density, it is possible to develop a graphite whisker with this density by changing the aspect ratio [5]. This advantage is important for preparing an electrode with high energy density (per volume). Moreover, as graphite whisker consists of concentric layers of basal plane graphite, this carbon is expected to be a material of which the destruction of the structure will not occur at lithium intercalation/de-intercalation. Therefore, graphite whisker is a material of interest as the carbon anode in lithium-ion rechargeable batteries. On the other hand, LiCoO₂ has been widely investigated as a cathode material in lithium-ion rechargeable batteries because of its high potential [6]. The batteries with LiCoO₂ cathodes and carbon anode are the so-called ‘rocking-chair system’ with a potential of 4 V.

In this work, electrochemical performances of graphite whisker and LiCoO₂ were investigated by galvanostatic charge/discharge examination. Further, a coin-type cell was prepared with these materials to study its performance as rocking-chair system.

2. Experimental

2.1. Performance of graphite whisker

Grasker heat-treated at 2800 °C was used. The diameter of this carbon was $\sim 2 \mu\text{m}$ and the length $\sim 10 \mu\text{m}$ (sample code: 2GWH-2A). 2GWH-2A was mixed with 10 wt.% of poly(vinylidene fluoride) (PVDF) in *N*-methyl-2-pyrrolidinone (NMP) to obtain a homogeneous paste. This paste was spread on a nickel sheet. This electrode was set in a three-electrode cell as the working electrode, after being dried at 120 °C under vacuum. Lithium metal was used as the counter and reference electrodes. 1 M LiClO_4 dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 volume ratio) was used as the electrolyte (battery grade, Mitsubishi Petrochemical Co.). The electrochemical performance was measured by galvanostatic charge/discharge examination. The current density was 25 mA/g carbon ($\sim C/15$) and the charge/discharge voltage was between 0 and 2.5 V (versus Li/Li^+). In this cell system, the carbon electrode always showed a higher potential than the lithium counter electrode. As the carbon electrode is dealt with the cathode, discharge means lithium insertion into the carbon electrode and charge means lithium de-insertion from the carbon electrode.

2.2. Performance of LiCoO_2

The cathode material was mixed with 10 wt.% of PVDF and 10 wt.% of acetylene black in NMP and was spread on a titanium sheet. The galvanostatic charge/discharge examination was performed in a three-electrode cell with 1 M $\text{LiClO}_4/\text{EC-DEC}$. The current density was 27 mA/g LiCoO_2 and the charge/discharge voltage was between 3.5 and 4.5 V (versus Li/Li^+).

2.3. 2GWH-2A/ LiCoO_2 rocking-chair system

A coin-type cell (type 2430, diameter 24 mm, thickness 3.0 mm) was prepared with 2GWH-2A anode, LiCoO_2 cathode and 1 M $\text{LiClO}_4/\text{EC-DEC}$ electrolyte. The components of the electrode were the same as for the working electrode in a three-electrode cell. The carbon or LiCoO_2 paste was dried to remove NMP; the anode and the cathode were prepared by pressing into a disk, at 20 kg/cm². A polyethylene film was used as the separator and a titanium sheet was used as conductor between the electrode and the case. The galvanostatic charge/discharge examination was performed at 0.5 mA/cm², between 3.2 and 4.2 V.

3. Results and discussion

3.1. Performance of 2GWH-2A

Fig. 1 shows the galvanostatic charge/discharge profiles of the 2GWH-2A electrode during the first cycle. The discharging curve gave a small shoulder attributed to the formation of a passivated film that appeared at $\sim 0.8 \text{ V}$ (versus Li/Li^+) as shown by other carbon electrodes. This reaction was irreversible as the charging curve and this shoulder never appeared during following cycles. Further, the discharging curve consisted of three plateaus at 200, 100 and 75 mV when well-graphitized carbon electrodes were used. These plateaus must be attributed to the intercalation of lithium into the carbon electrode, because the colour of this electrode changed from black to gold at 75 mV (formation of graphite-intercalation compound at the first stage) and the deposition of lithium occurred at -20 mV in this cell system [7]. Moreover, the charging capacity was 363 mAh/g carbon (nearly equal to the theoretical capacity as LiC_6). Although the crystallinity of 2GWH-2A was high ($d_{002} = 0.3359 \text{ nm}$, $L_c = 76.1 \text{ nm}$), the degree of AB stacking was $\sim 70\%$ lower than for ideal graphite [8]. It means that the capacity of 2GWH-2A is estimated to be 260 mAh/g carbon. As 2GWH-2A has some lattice disorders within the graphite crystal structure, this carbon electrode might show a higher capacity than the estimated capacity by the degree of AB stacking [7,8]. This phenomenon may be explained that 2GWH-2A has a new site of lithium storage. Fig. 2 shows the

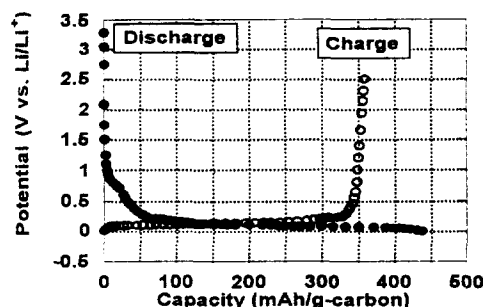


Fig. 1. Potential change of 2GWH-2A during the galvanostatic charge/discharge in the first cycle.

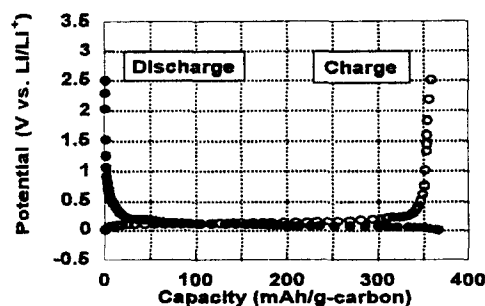


Fig. 2. Potential change of 2GWH-2A during the galvanostatic charge/discharge in the fourth cycle.

Table 1
The charge/discharge properties of LiMO_2 ($M = \text{Co}, \text{Mn}$ and Ni)

	1st cycle			3rd cycle		
	Capacity (mAh/g [*])		Coulombic efficiency (%)	Capacity (mAh/g)		Coulombic efficiency (%)
	Charge	Discharge		Charge	Discharge	
LiCoO_2	208	194	93	194	186	96
LiCoO_2	163	160	98	158	158	100
LiMn_2O_4	137	131	96	127	126	99
LiNiO_2	177	126	71	115	112	97

* Potential range = 3.0–4.3 V vs. Li/Li^+ .

charge/discharge profiles during the fourth cycle. The charging capacity was kept constant between the first and the fourth cycles, and the coulombic efficiency was close to 100%. It was confirmed by electrochemical examination that 2GWH-2A was a suitable carbon electrode with high energy density.

3.2. Performance of LiCoO_2

Fig. 3 shows the charge/discharge profiles of the LiCoO_2 electrode during the first cycle. In this Figure, LiCoO_2 electrode showed three plateaus near 4 V (versus Li/Li^+) and a high capacity (194 mAh/g LiCoO_2). Further, the LiCoO_2 electrode showed good stability during cycling (Fig. 4). To compare the performance with LiCoO_2 , LiMn_2O_4 and LiNiO_2 were also examined

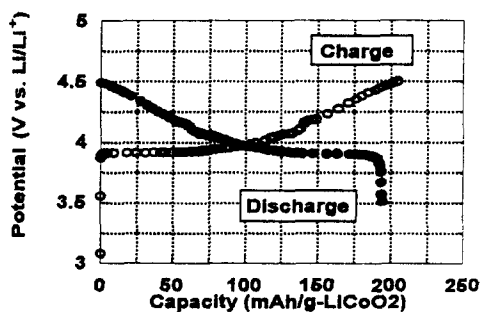


Fig. 3. Potential change of LiCoO_2 during the galvanostatic charge/discharge in the first cycle.

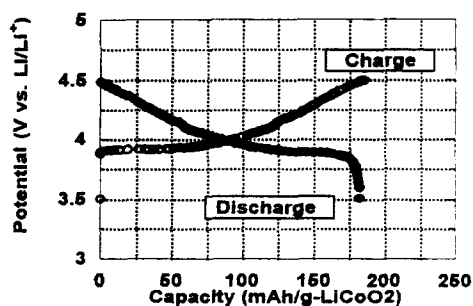


Fig. 4. Potential change of LiCoO_2 during the galvanostatic charge/discharge in the fourth cycle.

by charge/discharge tests. The charge/discharge results of cathode materials between the first and third cycles are summarized in Table 1. All cathode materials showed good stability during cycling; LiCoO_2 showed the highest capacity.

3.3. Performance of 2GWH-2A/ LiCoO_2 rocking-chair system

Fig. 5 shows the charge/discharge profiles of a coin-type battery prepared with 2GWH-2A and LiCoO_2 , during the first cycle. The initial potential of this cell was ~ 0 V and the potential was quickly increased up to 3 V. Further, a small shoulder appeared at near 3 V and the potential increased slowly to a plateau between 3.8 and 4.2 V. Fig. 6 shows the charge/discharge

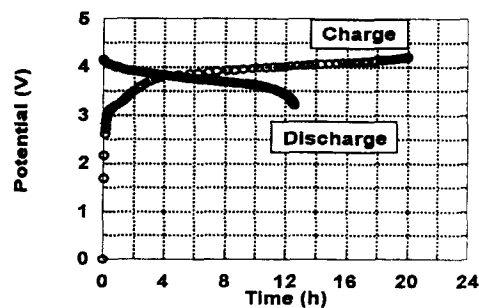


Fig. 5. Potential change of 2GWH-2A/ LiCoO_2 cell during the galvanostatic charge/discharge in the first cycle.

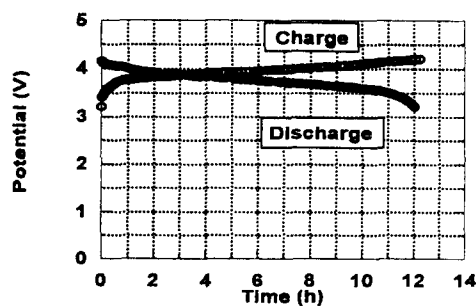


Fig. 6. Potential change of 2GWH-2A/ LiCoO_2 cell during the galvanostatic charge/discharge in the fifth cycle.

profiles during the fifth cycle. The small shoulder, as seen during the first cycle, did not appear at charging. Further, the coulombic efficiency was $\sim 100\%$; the discharging capacity was kept constant between the first and fifth cycles. From these results, 2GWH-2A/LiCoO₂ cell is expected to show a good stability during cycle life with high energy density. Moreover, the charge/discharge profiles of this coin cell suggest that the high potential depends only on the performance of the positive electrode, because the charge/discharge characteristics of the 2GWH-2A electrode show large plateaus near 0 V versus Li/Li⁺.

4. Conclusions

The results suggest that 2GWH-2A gives much higher capacity by optimization of the degree of structural disorders. Further, a coin cell based on 2GWH-2A has good a stability in cycle life and keeps a high potential; this carbon is excellent as the anode material in lithium-

ion rechargeable batteries. The electrochemical performance of this carbon electrode obtained with laboratory cells and coin-type cells can also be extrapolated to large-scale batteries.

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