

Design and performance of 10 Wh rechargeable lithium batteries

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Abstract

New metal–carbon composite anodes were developed by a chemical deposition method of metal particles onto graphite powder. Silver–graphite composites consisted of ultrafine silver particles on a graphite surface, exhibiting a large specific volume capacity of 468–505 Ah/l which may be due to Li–Ag alloy formation. The Ag–graphite anodes also showed excellent cycleability over 700 charge/discharge cycles with only 3% capacity loss. 10 Wh class rechargeable lithium batteries with energy densities of 270–300 Wh/l were manufactured using Ag–graphite anodes and cathodes of LiNiO₂ or LiCoO₂. Little capacity loss in these batteries was found even after 250 cycles because of the highly durable Ag–graphite anodes. © 1997 Elsevier Science S.A.

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1. Introduction

A government program developing dispersed battery energy storage systems has been in progress under a grant of the New Energy and Industrial Technology Development Organization (NEDO) since 1992. Under this program 20–30 kWh energy storage systems will be created before 2001 for application in load-leveling systems and electric vehicles. The battery energy storage system for load-leveling requires long life rechargeable lithium batteries which have energy densities of 240 Wh/l and 120 Wh/kg and charge/discharge cycles of more than 3500 at a 0.125C charge/discharge rate for the usage over ten years. Electrodes possessing excellent cycleability as well as high specific capacity are essential for creating long life batteries.

New metal–carbon composite anodes were developed to improve the cycleability of metal anodes which electrochemically alloy with lithium. Although metals such as Ag, Pb, Al, etc., have high theoretical specific weight capacities (200–800 Ah/kg), their capacities decrease with cycle number [1]. The capacity loss of metal anodes may result from the deterioration of the electrical contact among metal particles or grains due to a large volume change of metal crystals during charge/discharge cycles [2]. Silver–graphite composite (Ag–graphite) anodes were developed in order to

solve the capacity loss of metal anodes. The Ag–graphite anodes which consist of ultrafine Ag particles disseminating on the surface of graphite have improved cycleability and specific volume capacity in comparison with both the metal and the conventional graphite anodes. This paper describes the design and performance of 10 Wh rechargeable lithium batteries using Ag–graphite anodes and LiNiO₂ and LiCoO₂ cathodes.

2. Experimental

The Ag–graphite powder was produced according to the scheme given in Fig. 1. Water and ethanol were mixed in a vessel and heated to 50 °C on a hot plate. Salts of Ag⁺ ions such as AgNO₃ and graphite powder with weight ratios of 2.5/97.5–10/90 were added to the solution. Graphite powder was suspended in the solution with vigorous stirring by a magnetic stirrer. Then, a reducing agent such as HCHO, N₂H₄, etc., was added to the solution to reduce Ag⁺ ions and deposit ultrafine Ag particles on the graphite particles. A hydrated Ag–graphite composite powder was separated by filtration. Completion of the Ag⁺ reduction was checked by the AgCl precipitation test: adding HCl into the filtrate. After the powder was dried in vacuum, it was used for the preparation of Ag–graphite anodes as follows. The Ag–graphite powder was mixed with an organic solution containing

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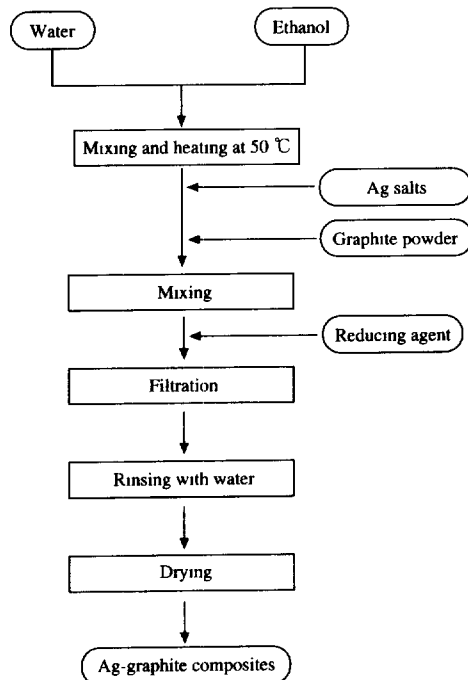


Fig. 1. Scheme of preparation of Ag-graphite composites by a chemical deposition method.

poly(vinylidene difluoride) (PVDF) binder, and the mixture was coated onto a copper foil. The weight ratio of Ag-graphite/PVDF was 90/10. The capacity of the Ag-graphite anodes was measured by a constant-current charge/discharge method between 0.01 and 1 V using lithium counter electrodes. The current was set at 120 mA for 1 g of Ag-graphite composites.

LiNiO₂ powder was prepared from Ni(OH)₂ and LiOH·H₂O by calcination at 750 °C in an oxygen atmosphere. LiCoO₂ powder (Nippon Chemical Industrial) was

used without any pretreatment. Mixtures of graphite, the organic solution containing PVDF and LiNiO₂ or LiCoO₂ were coated onto an aluminum foil to prepare the cathodes. Each cathode was covered with a polyethylene separator in envelop form.

The Ag-graphite anodes, and the LiNiO₂ or LiCoO₂ cathodes covered with separators were piled alternatively, and inserted into prismatic stainless-steel vessels of 80 mm × 8.9 mm × 60 mm (*H* × *D* × *W*) and a volume of 42.7 cm³. The sealed 10 Wh rechargeable lithium batteries were equipped with safety vents with two functions; (i) cutting off the output current of the batteries by a switch which works at a low internal pressure and (ii) liberating the gas accumulated in the batteries through a thin aluminum vent which ruptured at a high internal pressure. The electrolytic solutions in use were binary mixtures of ethylene carbonate (EC) and dimethyl carbonate (DMC) containing 1 M LiPF₆.

3. Results and discussion

3.1. Features of Ag-graphite composites

The surface morphology of the Ag-graphite composite powder, in which the Ag content was 10 wt.% (10% Ag-graphite), is presented in Fig. 2(a) by scanning electron microscopy (SEM).

Very small white spots were highly dispersed on the surface of graphite particles. The spots were identified as Ag by energy dispersed X-ray analysis (Fig. 2(b)). X-ray diffraction observation of the 10% Ag-graphite powder revealed that Ag existed in a metallic state, but not in an oxidized one (data are not shown). The diameter of the Ag particles were in the range of 10–100 nm. Highly dispersed Ag metal on the

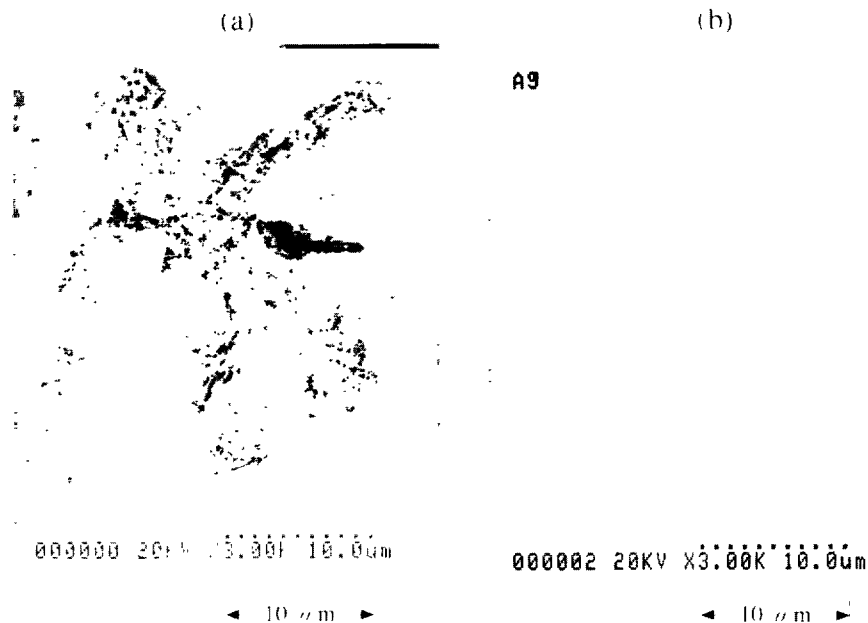


Fig. 2. (a) Scanning electron micrograph of Ag-graphite composite particles, (b) the corresponding Ag distribution map of energy dispersed X-ray analysis.

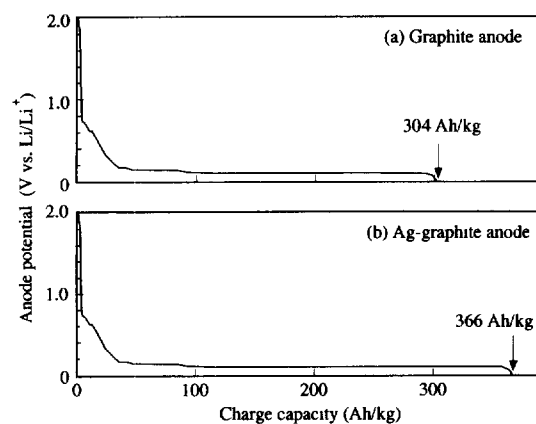


Fig. 3. Charging curves of (a) graphite and (b) Ag-graphite anodes in 1 M $\text{LiPF}_6/\text{EC-DMC}$ solutions, Ag content of Ag-graphite anode 10 wt.%, current density; 120 mA for a unit weight of the graphite and the Ag-graphite composites.

graphite may act as an electron conductor to enhance the Li-intercalation reaction on graphite because of its extremely low resistance ($1.59 \mu\Omega \text{ m}$). In addition, Ag can electrochemically alloy with lithium to form LiAg alloy, which may increase the capacity of anodes.

Fig. 3 illustrates the typical first charging curves of the graphite and the Ag-graphite anodes at a constant current density of 120 mA for the weight of Ag-graphite composites. The charging cutoff voltage was set at 0.01 V. Although the charging curve of the Ag-graphite exhibited a similar form compared with that of the graphite, the capacity of the Ag-graphite increased by 62 Ah/kg over the graphite.

Table I presents the specific discharge capacities of the graphite and the Ag-graphite anodes which were prepared using 10 wt.% PVDF binder and pressed at 0.5 t/cm^2 . The capacity measurement was conducted at 120 mA for weights of graphite or Ag-graphite composites between 0.01 and 1.0 V versus lithium counter electrodes. The specific volume capacities of the Ag-graphite anodes were larger than that of the simple graphite anode, whereas the former specific weight capacity was almost comparable with the latter one. The calculated specific volume capacity, assuming the closest packing of 10% Ag-graphite particles in the anodes, was 962

Table I
Specific discharge capacities of graphite and Ag-graphite anodes ^{a,b,c}

Ag content (%)	Density (g/cm^3)	Specific capacity	
		(Ah/kg)	(Ah/l)
0	1.25	310	388 (685)
2.5	1.43	327	468 (790)
5.0	1.53	330	505 (865)
10.0	1.55	317	491 (962)

^a Specific volume capacities given in parentheses are the calculated values, assuming the closest packing of PVDF and graphite or Ag-graphite particles.

^b The charge and discharge current densities, 120 mA for a unit weight of the graphite or the Ag-graphite composites.

^c The working voltage 0.01–1.0 V against a lithium counter electrode.

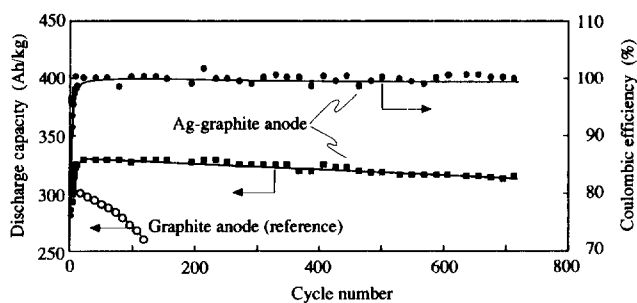


Fig. 4. Discharge capacity and the coulombic efficiency of an Ag-graphite anode as a function of cycle number; Ag content of Ag-graphite anode: 10 wt.%. (■) discharge capacity for the Ag-graphite anode; (●) coulombic efficiency for the Ag-graphite anode, and (○) discharge capacity for the graphite anode.

Ah/l, which was 40% higher than that of the graphite anode. The capacity increase of the Ag-graphite composites may be attributed to the Li-Ag alloy formation as well as the electron conductivity enhancement.

Fig. 4 is the cycle test data of the 10 wt.% Ag-graphite anode. The capacity increased in the initial stage of the cycle test. The cycleability became very stable over 700 cycles with 3% in capacity loss and 99–101% in the coulombic efficiency. The cycleability and the specific capacity of the graphite anode prepared from the original graphite powder were noticeably inferior to those of the Ag-graphite anode. This result indicates that ultrafine Ag particles markedly enhance the cycleability of the anodes with a negligible capacity loss. The improved cycleability may be attributed to an Ag-enhanced electron conduction between the graphite particles, because of the low resistance of Ag (Fig. 2).

3.2. Performance of rechargeable lithium batteries of the Ag-graphite/LiNiO₂ and Ag-graphite/LiCoO₂ systems

Prismatic sealed 10 Wh rechargeable lithium batteries were manufactured with Ag-graphite anodes and cathodes of LiCoO₂ or LiNiO₂ in a full charge/discharge mode: the batteries were charged and discharged up to a depth-of-discharge (DOD) of 100%. The charge and discharge rates were set at 0.125C. Fig. 5(a) shows the charging and discharging curves of the Ag-graphite/LiCoO₂ system. The discharge capacity, the specific energy and the average discharge voltage for this system were 3.05 Ah, 11.5 Wh and 3.77 V, respectively. The specific volume and weight energy densities were estimated to be 270 Wh/l and 90 Wh/kg. In the case of the Ag-graphite/LiNiO₂ system (Fig. 5(b)), the average discharge voltage decreased to 3.6 V. However, specific energy densities of this system rose to 300 Wh/l and 110 Wh/kg, respectively, because of the larger specific capacity density of LiNiO₂.

Fig. 6 exhibits the cycleability of the Ag-graphite/LiCoO₂ and Ag-graphite/LiNiO₂ systems at a 0.125C charge/discharge rate. In this paper, we assumed that the cycle life of rechargeable lithium batteries ends at a number of cycles when the discharge energy decreases to 70% of the initial

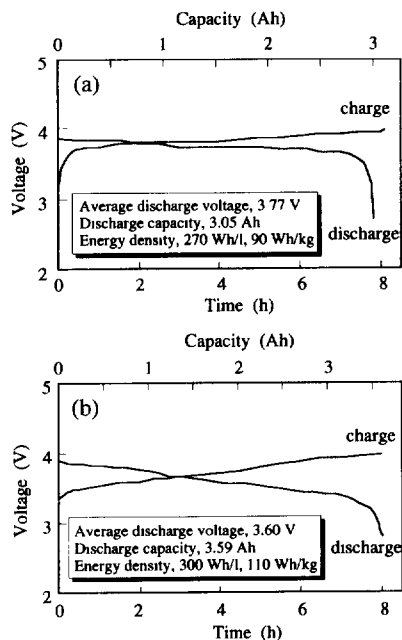


Fig. 5 Charging and discharging curves of 10 Wh rechargeable lithium batteries: (a) Ag-graphite/LiCoO₂ system, and (b) Ag-graphite/LiNiO₂ system

value. According to this assumption, when the discharged energy measured at 100% DOD will decrease to that obtained at 70% DOD, the number of cycles represents the cycle life when 70% of the initial battery energy is retained. A charge/discharge cycling test at 100% DOD was conducted for the batteries at intervals of 50 cycles to measure the battery energy retained. During the other cycles, the batteries were charged and discharged up to 70% DOD. The discharge energy loss was not noticeable even after 700 and 350 cycles for the Ag-graphite/LiCoO₂ or the Ag-graphite/LiNiO₂ systems, respectively.

4. Conclusions

Sealed 10 Wh rechargeable batteries were manufactured using newly developed Ag-graphite composite anodes which possessed excellent cycleability; the capacity loss was only 3% over 700 cycles. The Ag-graphite/LiCoO₂ system has a high energy density of 270 Wh/l. The use of Ag-graphite anodes and LiNiO₂ cathodes had created 300 Wh/l energy batteries. Both systems exhibited good cycleability over 700

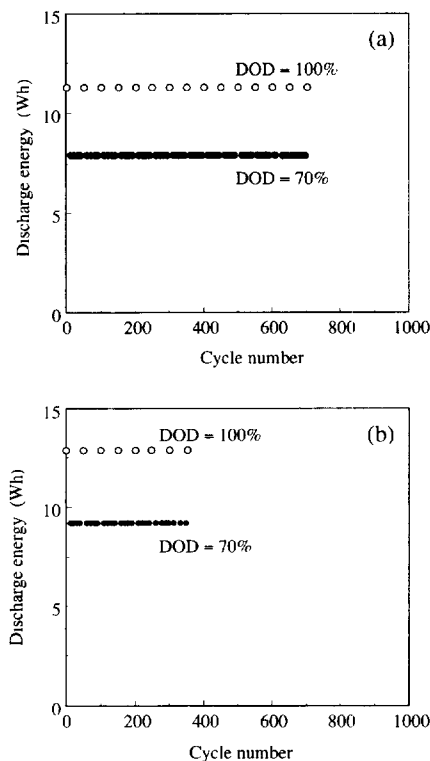


Fig. 6 Cycleability of 10 Wh rechargeable lithium batteries (a) Ag-graphite/LiCoO₂ system, and (b) Ag-graphite/LiNiO₂ system (○) discharge energy measured by the cycle test of 100% DOD at intervals of 50 cycles, and (●) discharge energy measured by the cycle test of 70% DOD at the other cycles. The energy densities of the both systems at 100% DOD are the same values as given in Fig. 5.

and 350 cycles, respectively, at charge and discharge rates of 0.125C.

Acknowledgements

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