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Rechargeable molecular cluster batteries

Hirofumi Yoshikawa,[a] Chieko Kazama,[a] Kunio Awaga,*[a] Masaharu Satoh[b] and Jun Wada[c]

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We fabricated a rechargeable molecular cluster battery, based on a cathode active material, $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$. The charging–discharging experiments revealed rechargeable battery performance with a capacity of *ca.* 90 A h kg^{-1}, while the first discharging process exhibited an extremely high value of 200–250 A h kg^{-1}.

In recent years, increasing energy demands and concerns over the global environment have led to a greater focus on renewable energy sources, such as batteries with high efficiency and capacity. At present, lithium ion batteries are widely used as rechargeable batteries, due to their high capacity and good cycle performance.[1,2] Lithium is useful in batteries because of its lightness and because of the high voltage of the redox reaction between Li and Li^+. In lithium ion batteries, a layered compound, $LiCoO_2$, is utilized as a cathode. Although this material can provide high capacity, the charging/discharging of the lithium ion batteries is slow because these processes include the adsorption/desorption of lithium in the layered material. In addition, cobalt is toxic and expensive, so much effort has been devoted to the development of low-cost, environmentally friendly cathode materials which realize quickly chargeable, high-power-density batteries.

Recently, organic radical batteries have been developed as a new type of rechargeable lithium battery, in which organic polymers carrying stable nitroxyl radicals are utilized as a cathode active material.[3–5] Because of the smooth and fast electrochemical reactions of the organic radicals, the organic radical batteries are chargeable/dischargeable with a high current density in a short time. However, their capacities (<100 A h kg^{-1}) are lower than those of the lithium ion batteries (180 A h kg^{-1}) because the rather large radical moiety (molecular weight = *ca.* 200) can store only one or two electrons in the redox reaction. To achieve both high capacity and fast charging/discharging, it would be useful to adopt molecule-based compounds undergoing multi-step redox reactions as a cathode active material.

The chemistry of the molecular metal clusters, small aggregates of metal ions connected by (organic) ligands, has been well researched in the last two decades.[6] Some of these clusters are high-spin species that have attracted much attention as potential single molecule magnets in the field of molecular magnetism; the magnetic relaxation of these magnetic clusters becomes slow enough that their magnetization curves exhibit a hysteresis loop like that of conventional ferromagnets.[7,8] In the present work, we have fabricated a molecular cluster battery in which the cathode active material is a molecular cluster, $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ (abbreviated as Mn12), that is stable and insoluble to most solvents and exhibits a multi-step redox reaction. Mn12 is the best-known single molecule magnet, and many chemical modifications have already been made to it.[9]

The cartoon in Fig. 1 schematically shows the structure of the molecular cluster battery. The cathode was prepared as follows: 10 mg of Mn12 and 80 mg of VGCF (carbon fiber prepared in the gas-phase; Showa Denko Co., Tokyo, Japan) were mixed with 10 mg of a binder, polytetrafluoroethylene resin (POLYFLON; Daikin Industries, Ltd., Osaka, Japan), and then the mixture was spread onto an aluminium plate and dried. Fig. 1 shows an SEM image of the cathode; it looks as if a microcrystal of Mn12 was electrically wired with VGCF. The anode material was lithium metal that was isolated from the cathode by a separator (polyolefin film). The cathode and anode were placed in a coin-shaped cell with an electrolyte and a mixed solution of diethyl carbonate (DEC) and ethylene carbonate (EC) (DEC : EC = 7 : 3) in an inert atmosphere.

Fig. 2 shows the charge–discharge curves for the fabricated Mn12–Li battery at a constant current density of 0.01 mA cm^{-2} in the voltage range of 2.0–4.0 V. When we tried to charge this as-prepared cell, the initial voltage was very high (3.8 V) and was quickly increased to more than 4 V (black curve). This battery was already charged during the fabrication process. In fact, it exhibited a discharging process (red curve); the voltage exhibited a plateau at 3.4 V after an initial drop, followed by a decrease to

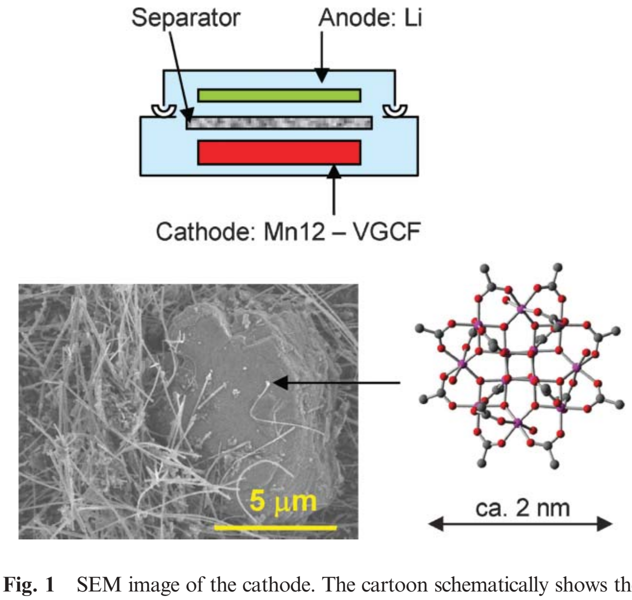

Fig. 1 SEM image of the cathode. The cartoon schematically shows the structure of the Mn12–Li molecular cluster battery.

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[a] *Research Center for Materials Science & Department of Chemistry, Nagoya University, Furo-cho, Chikusa, Nagoya, 464-8602, Japan. E-mail: awaga@mbox.chem.nagoya-u.ac.jp; Fax: +81-52-789-2484; Tel: +81-52-789-2487*
[b] *Nano Electronics Research Laboratories, NEC Corporation, Miyukigaoka 34, Tsukuba, Ibaraki 305-8501, Japan*
[c] *Corporate Planning Department, Nippon Kasei Chemicals Co., Ltd., 1-8-8 Shinkawa, Chuo-ku, Tokyo, 104-0033, Japan*

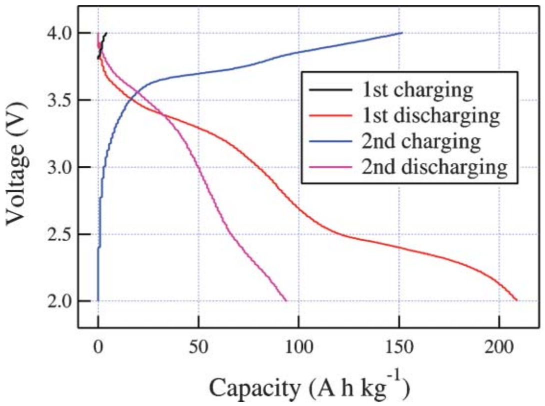

Fig. 2 Charging–discharging curves of the Mn12–Li molecular cluster battery.

a second plateau at 2.5 V. Finally the voltage collapsed, and an extremely large capacity of more than 200 A h kg^{-1} was recorded. This value was larger than that of the Li ion battery.

The blue and pink curves in Fig. 2 indicate the second charging and discharging processes, respectively. In charging, the voltage quickly increased to a plateau at 3.7 V, followed by a gradual increase. This battery was chargeable after the first discharging. In discharging, the voltage gradually decreased, formed a shoulder at 3.5 V, and became less than 2.0 V, indicating a capacity of *ca.* 90 A h kg^{-1}. This value was much lower than that for the first discharging, but was comparable to those of the organic radical batteries.[3–5] The features of the charging–discharging curves in the third run or later were similar to those of the second run.

The cycle performance for the charging–discharging processes was examined in the range of 2.0–4.0 V. The results are shown in Fig. 3. Only the first run indicated a large capacity above 200 A h kg^{-1}. We have confirmed the reproducibility of the first run anomaly by remaking the coin-shaped batteries several times; all the samples exhibited large capacities of 200–300 A h kg^{-1} in the first run. After the second run or later, the capacity was maintained at 75 A h kg^{-1}, though it tended to decrease slightly. To our knowledge, this is the first rechargeable molecular cluster battery based on a molecular metal cluster.

We calculated the theoretical value of the capacity for the present Mn12–Li battery. If one Mn12 cluster molecule stores one electron, the capacity would be 14 A h kg^{-1}. Therefore, the capacity in the second run or later can be explained by assuming that one Mn12 molecule stores a few electrons. However, it might be hard to rationalize the large capacity in the first run. It is possible that the electrons were accumulated in the surfaces of the microcrystals of Mn12, as well as in the molecules. Although it was hard to explain the difference between the first run and the later ones, molecular cluster species, such as Mn12, can act as cathode active materials. Since there are numerous molecular metal clusters which stably exhibit multi-step redox reactions,[10] and since it is not very difficult to control the redox potentials by means of chemical modification,[9] the study of the molecular cluster battery should grow to become a major branch of the research into rechargeable batteries.

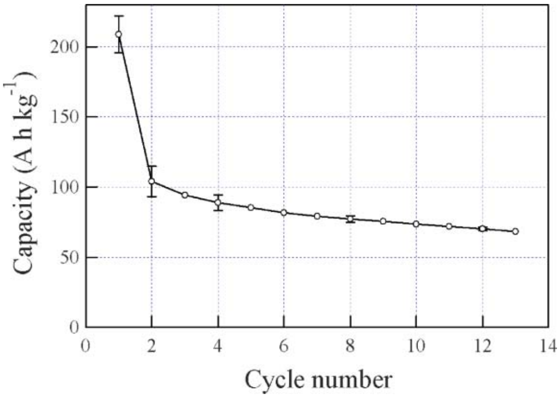

Fig. 3 Cycle performance of the Mn12–Li molecular cluster battery.

In this communication, we described the results of charging–discharging experiments with a current density of 0.01 mA cm^{-2}, which is lower than that for conventional batteries. When we carried out fast charging–discharging experiments with 1 mA cm^{-2}, the capacity decreased rather quickly during the repeated charging–discharging processes, due to the chemical decomposition of Mn12. The slow rate of the charging–discharging reactions for the present Li–Mn12 battery was probably caused by the fact that the charging–discharging was necessarily accompanied by movements of electrons in the insulating microcrystals of Mn12. To achieve the fast charging–discharging that we expect in a molecular cluster battery, it would be necessary to improve the electrical connections between Mn12 and the cathode electrode.

In summary, we fabricated a molecular cluster battery using Mn12 as a cathode active material. The battery was rechargeable, but fast charging–discharging was not achieved due to the chemical decomposition of Mn12. While the first run capacity was extremely high, the moderate capacity in the second run was attributable to the multi-step electrochemical reactions of Mn12. We believe that the present work will open a new branch of research into rechargeable molecular cluster batteries.

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