

Development of Organic Radical Battery

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Abstract

The organic radical battery is a secondary battery using a plastic material containing stable radicals. It charges and discharges by the oxidation and reduction of radical species such as a nitroxyl radical. This battery features a high-power discharge capability and a flexible structure. In a high-power pulse discharge test, the thin organic radical battery presented no degradation in cell resistance even after 10,000 times of continuous pulse discharge (1-second pulses). The thin and flexible organic radical battery is considered particularly suitable for supplying power to compact ubiquitous devices in the future such as the highly functional smart card.

Keywords

secondary battery, organic cathode, stable radical, high power, thin battery, charge storable plastic

1. Introduction

Portable information devices such as mobile phones and laptop PCs have now become indispensable for our daily life and business. This is mainly the outcome of the reduced size and improved performance with high functionality of semiconductor chips, but advances such as the increased capacity of lithium-ion batteries used as power supplies have also contributed considerably to the advancement of such devices. It is expected that portable information devices will continue to advance and new devices with new features such as wearability and flexibility will be released in the future. In turn, secondary batteries used as power supplies are expected to offer various other properties, such as a thin structure, flexibility and higher power, in addition to large capacity.

Secondary batteries typically employ compounds of heavy metals such as lead, cadmium, nickel or cobalt as electrode materials, but new electrode materials are also being developed. As part of these efforts, active research is being conducted into the organic electrode for the secondary battery because of their light weights and the expectations of implementing various properties by means of molecular design. NEC has been developing organic charge storage materials since the 1990s. It was found that the plastic containing stable radicals present excellent charge storage characteristics. We propose a secondary battery based on them under the name “organic radical battery”¹⁾. Here, “radicals” refers to unpaired electrons, which are in general extremely unstable. When attempting to store electricity in an organic compound, it generates unstable ionic radicals. However, these decompose immediately after the generation. This property makes it impossible to store

electricity in the organic compounds. To solve this problem, we focused on very special kinds of organic compounds that include stable radicals, which have unpaired electrons with long-term stability. When a stable radical compound stores electric energy, unpaired electrons disappear and become ionic molecules, which can be stabilized with a combination of proper counter ion. The organic radical battery is a secondary battery which charges and discharges by the redox between stable radical compounds and stable ionic molecules.

2. Energy- Storing Plastic – Stable Radical Polymer

The existence of stable radical compounds has long been known, but there has been no attempt to apply them to battery technology. Neither has there been any report on the stability of the oxidation and reduction required for the materials of secondary battery electrodes. NEC conducted a basic electrochemical evaluation of various stable radical compounds and found that 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) containing nitroxyl radical (NO radical) (Fig. 1) has excellent stability in a repeat of oxidation-reduction. TEMPO is capable of repeating stable oxidation-reduction between NO

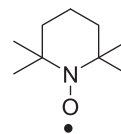


Fig. 1 2,2,6,6-tetramethylpiperidine-*N*-oxyl (the black dot represents an unpaired electron).

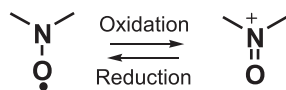


Fig. 2 Oxidation-reduction of a nitroxyl radical.

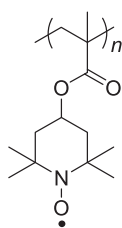


Fig. 3 PTMA

radical and oxoammonium (NO cation) (**Fig. 2**). The voltage of its oxidation-reduction is relatively high (about 3.6 V vs. Li/Li^+) and it is comparable to the voltage of a lithium-ion battery. Later, in an electrochemical kinetic study, it was also found that TEMPO has an extremely high oxidation-reduction rate, which means that TEMPO has the potential to discharge at a large current, so that it can be the electrode material for a high-power battery. Aiming at developing high-power batteries, we are presently using materials with a TEMPO structure as cathode materials for an organic radical battery.

An electrode material must be insoluble to electrolyte. However, all commercial stable radical materials have been low-molecular substances that dissolve easily into the electrolyte. Therefore, to prevent TEMPO from being dissolved in electrolyte, we synthesized a plastic (polymer) with a TEMPO structure, considering the fact that polymers usually have lower solubility than low-molecular substances. We synthesized a polymer with a polymethacrylate skeleton and TEMPO structure, poly (4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl) (PTMA) ¹⁾ (**Fig. 3**). PTMA can be synthesized in relatively few steps from relatively low-cost materials and is therefore advantageous from the viewpoint of manufacturing costs.

Although radicals are usually extremely unstable, those of PTMA showed very high stability. We evaluated the time degradation of radicals by measuring the spin concentration (radical concentration) of the polymer on the electron spin resonance (ESR) spectrum and did not observe a reduction in electron spin even after the polymer was left in a room atmosphere for half a year. When actually applied as a battery material, PTMA is stable on the order of years. Even when

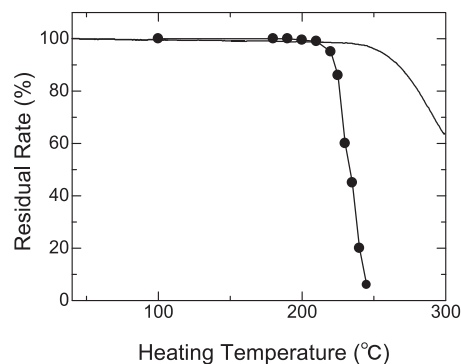


Fig. 4 Pyrolysis rate (curve) of PTMA (temperature rise rate 10 degrees C/minute) and residual radical rate after 1 minute of heating (•).

PTMA that had been synthesized more than three years earlier was used as an active electrode material, the charge-discharge was possible without degradation in battery characteristics. **Fig. 4** shows the thermogravimetric analysis (TGA) curve of PTMA and the residual radical rate measured on the ESR spectrum after one minute of heating at a specified temperature. The TGA indicates that the polymer structure is stable up to 220°C and the ESR measurement after heating does not show any deactivation of radicals up to 200°C. These results indicate that PTMA is excellent in long-term storage stability and thermal stability.

Radical molecules store charges in the radical structures. Consequently, the quantity of electricity stored per unit weight (capacity density) is determined by the molecular weight per radical. When one electron is stored per radical, the theoretical capacity of PTMA is 111 mAh/g, which corresponds to 80% of the storage capacity of the positive-electrode material of a lithium-ion battery. (The capacity density of LiCoO_2 used as the electrode material of a lithium-ion battery is 140 mAh/g.)

3. PTMA/Carbon Composite Electrode

An electrode material must be insoluble to electrolyte because an electrode cannot store electricity if its materials are eluted into the electrolyte and the eluted material will degrade battery characteristics considerably. PTMA has very low solubility in representative nonaqueous electrolytes such as diethyl carbonate and acetonitrile. Nevertheless, in applying it as a battery material, we turned it into a perfectly insoluble material by introducing cross-linking structures between the

Development of Organic Radical Battery

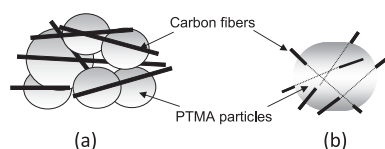


Fig. 5 (a) PTMA/carbon electrode obtained by normal process (concept) and (b) PTMA/carbon complex (concept).

main polymer chains (cross-linked PTMA) in order to prevent dissolution of even a small amount after long use or under high temperatures.

PTMA is an aliphatic polymer and is not electrically conductive by itself. While the TEMPO structure has the capacity to store electricity, it is not capable of handing electrons to the electricity storage section. Since PTMA cannot be used as the sole material for a battery electrode, because this would result in large resistance, we mixed an electro-conductive material into the electrode. This electrically-conductive material is the carbon that is already in use as the electrically-conductive additive to lithium-ion batteries. The selection of the type of carbon used here is important for obtaining high power output because it has a great effect on the resistance of the electrode. As a result of the study of various carbon materials, we found that a vapor-grown carbon fiber (VGCF) as thin as 150 nm in diameter is effective for reducing electrode resistance. This is because this material has relatively high electrical conductivity and its extremely small in diameter increases the area of contact with the radical material. With a PTMA/carbon electrode, the fabrication process noticeably affects battery characteristics. An ordinary electrode is usually fabricated by dispersing the constituents in a solvent and applying and drying the solvent to a metallic foil. When this fabrication process is applied to a PTMA/carbon electrode, carbon fibers are attached around the PTMA particles (Fig. 5 (a)). As the PTMA particles in this structure do not include the electro-conductive materials for exchanging electrons, battery resistance would become high in the charge and discharge. So instead we kneaded carbon into PTMA swelled with organic solvent to fabricate a PTMA/carbon complex in which carbon is caught inside PTMA particles (Fig. 5 (b)) and used this as an electrode material.

4. Characteristics of a Thin Type Organic Radical Battery

We evaluated the characteristics of a thin type organic

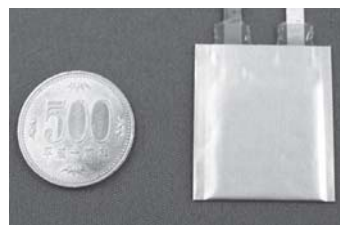


Photo 1 External view of a thin type organic radical battery.

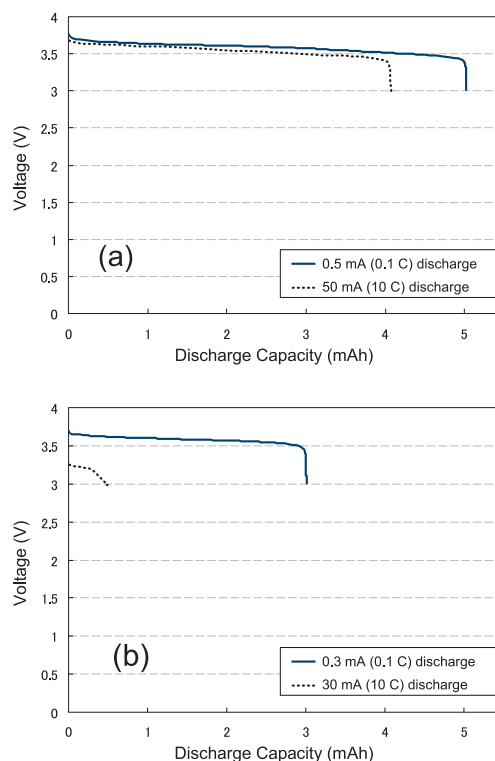


Fig. 6 Discharge curves of (a) an organic radical battery fabricated from PTMA/carbon complex and (b) an organic radical battery fabricated without using PTM

radical battery fabricated with PTMA/carbon complex²⁾. This thin organic radical battery (26 mm(V) × 24 mm(H)) (Photo 1) is fabricated by stacking PTMA/carbon complex electrodes, polyolefin separators and carbon negative electrodes, adding ethylene carbonate/diethyl carbonate mixed solvent containing 1M-LiPF₆ as an electrolyte and sealing all of these within aluminum laminate. Fig. 6 (a) shows the results of the discharge of a thin type organic radical battery at current of 0.5

mA and 50 mA. The discharge curve presents high voltage-flatness in the 0.5 mA discharge, with an average voltage of 3.6 V and a discharge capacity of 5 mAh. This high voltage-flatness is maintained even in a discharge at a relatively high current of 50 mA, and the discharge capacity in this case is 4.1 mAh (82% of the 0.5 mA discharge). Fig. 6(b) shows the discharge curve of an organic radical battery fabricated without using the complex. The discharge capacity in the 0.3 mA discharge is 3 mA, which is about 60% of the capacity in the 0.5 mA discharge of the organic radical battery using the complex. In the 30 mA discharge, the discharge capacity drops precipitously to 0.5 mAh. These results demonstrate that using PTMA/carbon complex can increase battery capacity and also enable discharge at a higher current.

Many electronic devices require a high pulse-power supply. This is required, for example, in the rewriting of electronic paper, the operation of sophisticated LSI-handling encryption and light emission from high-intensity LEDs. To deal with this requirement, we conducted pulse discharge testing at 20°C (pulse discharge time: 1 second) and obtained the results shown in Fig. 7. The maximum output power achieved in the 1-second pulse discharge test was 2.5 W at a discharge current of 1.2 A. At this time, the discharge current per electrode area was 113 mA/cm² and the output power per electrode area was 0.24 W/cm². The output density of this battery, calculated based on cell volume, is 9.5 kW/L excluding the aluminum laminate material or 5.7 kW/L including it. This output power per volume is at a level equivalent to the electric double-layer capacitor that is known to be one of the highest-powered commercially available energy devices. We also evaluated

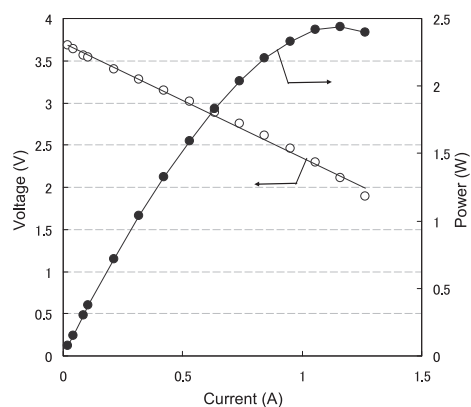


Fig. 7 Output characteristics of the organic radical battery (1-second pulse discharge).

stability under repeated pulse discharge by repeating a 1-second, 100 mA discharge every minute for 10,000 cycles. The results of this test, shown in Fig. 8, show that cell resistance barely increases after 10,000 cycles of pulse discharge and capacity does not decrease at all. These results demonstrate that the organic radical battery has high stability under repeated pulse discharge.

PTMA is levigated (becomes gel-like) when it absorbs electrolyte (Photo 2 (Left)). In the organic radical battery, therefore, a PTMA/carbon complex electrode also becomes a gel-like electrode containing carbon fibers. The electrode taken from the battery is very flexible, with no cracks observed even after repeated bending (Photo 2 (Center)). It is a rugged electrode, thanks to the carbon fibers playing the role of skeleton. The battery itself is also flexible (Photo 2 (Right)) and no change in battery characteristics was observed after repeatedly bending.

The above property of the battery may make it suitable for use as a power supply for devices that must be stable against bending, such as IC cards and wearable devices. Even if the

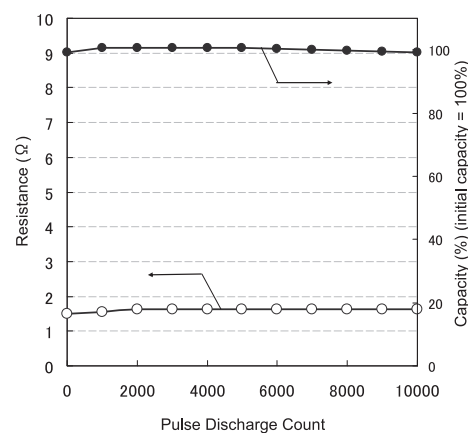


Fig. 8 Pulse cycle characteristics of the organic radical battery.

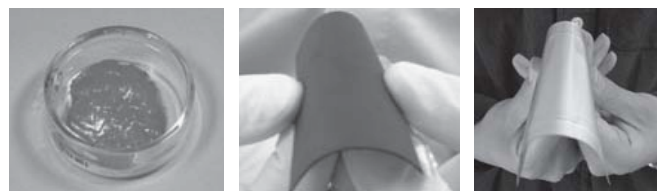


Photo 2 Electrolyte-permeated PTMA (left), electrode (center), thin type organic Radical battery (right).

Development of Organic Radical Battery

battery is shorted out by driving a nail through it, it is safe because intense temperature rise will not occur. The use of such a thin power supply with IC cards is expected to improve their functionality such as a display. If the battery is incorporated into clothes, it will be possible to include a display, communication device, etc.

5. Conclusion

NEC proposed and is currently developing an organic radical battery that uses a stable radical compound as the electrode material. An organic radical battery using electrodes made of a complex of radical polymer PTMA and carbon fibers has advantages such as high power, flexibility and safety. A thin type battery is considered to be suitable for use as a power supply for compact ubiquitous devices such as highly functional smart cards and wearable devices. We will verify the practicality of our development and aim to apply it as a power supply for the information terminals of the future.

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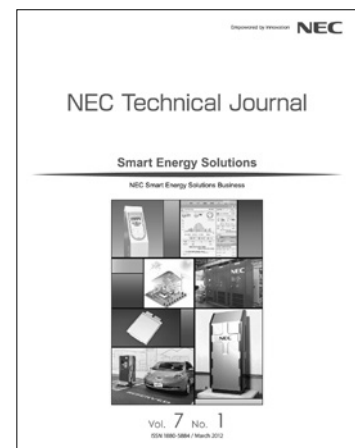
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March, 2012

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