

Short communication

# Cell properties for modified PTMA cathodes of organic radical batteries

Kentaro Nakahara<sup>a,\*</sup>, Jiro Iriyama<sup>a</sup>, Shigeyuki Iwasa<sup>a</sup>, Masahiro Suguro<sup>a</sup>,  
Masaharu Satoh<sup>a</sup>, Elton J. Cairns<sup>b</sup>

<sup>a</sup> Fundamental and Environmental Research Laboratories, NEC Corporation, Tsukuba, Japan

<sup>b</sup> Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, CA, USA

Received 20 April 2006; received in revised form 24 November 2006; accepted 28 November 2006

Available online 8 January 2007

## Abstract

Stable nitroxyl radical polymers, such as poly (2,2,6,6-tetramethyl-1-piperidinyloxy-4-yl methacrylate) (PTMA), are known to be effective as cathode active materials for lithium rechargeable batteries. A water-based slurry was used to prepare PTMA composite electrodes, enabling successful production of homogeneous electrodes. This improved utilization of active material and enabled us to obtain specific capacities almost equal to the theoretical value (111 mAh g<sup>-1</sup>). Lithium half cells were fabricated using these electrodes and using graphite as the anode active material, and their cycling stability, temperature dependence, rate capability and self-discharge rate were measured in detail. Although they showed 24% irreversible capacity on the first cycle, the capacity stabilized after the second cycle.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Organic radical battery; Lithium battery; Stable radical; PTMA

## 1. Introduction

Organic radical batteries are a new type of lithium rechargeable battery that utilizes reversible redox reactions of stable radical compounds as their cathode reaction. So far, a number of stable nitroxyl radical polymers, such as poly (2,2,6,6-tetramethyl-1-piperidinyloxy-4-yl methacrylate) (PTMA) [1,2] and poly (*N-tert*-butylnitroxyl-3,5-phenylene), have been synthesized and used as cathode active materials in lithium batteries [2,3]. There has been a lot of research on Li/PTMA as a material for rechargeable cells with a long cycle life [3–5], focusing particularly on its reaction mechanism.

Because PTMA lacks electronic conductivity, in previous work, we made a PTMA–carbon composite cathode by mixing and solidifying PTMA powder, carbon black, and PTFE binder. Using a composite cathode made with this process, we produced a rechargeable cell with a long cycle life [3]. However, the electrode's measured specific capacity was less than 80% of

the theoretical capacity, meaning that it was not homogeneous enough to achieve high utilization [3].

In the present study, our cathode preparation process used a doctor blade method with a water-based slurry, and we succeeded in making a homogeneous electrode with PTMA powder and in achieving a high utilization of the active material. The measured capacity was almost equal to the theoretical value. In addition, half-cell properties such as cycling stability, temperature dependence, rate capability and self-discharge rate were measured in detail. Our results also indicate that a graphite anode can be used with the PTMA based cathode, suggesting that the battery has great commercialization potential.

## 2. Experimental equipment and procedures

We synthesized PTMA in our laboratory by carrying out a radical polymerization of 2,2,6,6-tetramethylpiperidine-4-yl methacrylate monomer (LA-87, Asahi-denka) using 2'-azobisisobutyronitrile (AIBN) and then oxidizing it with 3-chloroperoxybenzoic acid (m-CPBA). The synthesis procedure is described in detail elsewhere [2]. All electrolytes were obtained from Ube Industries Ltd.

The PTMA cathode was prepared using the following procedure. To a make viscous solution, we dissolved 5.0 g of carboxy

\* Corresponding author at: Fundamental and Environmental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibarakizos-8501, Japan. Tel.: +81 29 850 1556; fax: +81 29 850 2635.

E-mail address: [k-nakahara@ak.jp.nec.com](mailto:k-nakahara@ak.jp.nec.com) (K. Nakahara).

methyl cellulose, CMC, (HB9, ZEON Corp.) in 500 g of pure water. Then, 1.25 g of PTFE fine powder (60% water dispersion, D-1B, DAIKIN) and 56.25 g of vapor grown carbon fibers (VGCF<sup>TM</sup>, Showa-Denko) were added to the CMC solution and intensively stirred for 1 h. Finally, 62.5 g of PTMA fine powder was added to the well-dispersed carbon ink and mixed well. The resulting slurry was spread on carbon-coated aluminum foil using the doctor blade method. After the solvent water was evaporated by heating (100 °C, 10 min), the PTMA cathode was complete. This cathode contained PTMA (50 wt.%), VGCF (45 wt.%), CMC (4 wt.%), and PTFE (1 wt.%) and was 130–180 μm thick. A mesocarbon microbead (MCMC, Osaka-gas) anode made of small particle size graphite (3 μm) was prepared by the usual process, using an NMP slurry and the doctor blade method. This anode contained graphite (90 wt.%), conductive carbon black (1.0 wt.%), and PVdF (9.0 wt.%). Its thickness was adjusted to 10–20 μm, and it was observed using a scanning electron microscope (SEM) (S-4100, HITACHI, SEM apparatus). A cyclic voltammogram was obtained using a standard three-electrode cell in a dry argon atmosphere at room temperature using an Electrochemical Analyzer 604, CH Instruments, potentiostat system. A platinum wire was used as the counter electrode, and a lithium metal electrode was used as the reference. The electrolyte was 1.0 M lithium hexafluorophosphate (LiPF<sub>6</sub>) in ethylene carbonate (EC) and diethyl carbonate (DEC) mixed solvent (EC/DEC = 3/7, v/v). The sweep speed was set to 1 mV s<sup>-1</sup>.

Coin cells (2320-type) were assembled using Celgard 2400 microporous film separators, in a dry room (dew point < -50 °C). In half-cell experiments, 1.4 mm thick lithium metal disks were used as anodes. As a liquid electrolyte, we used 1.0 M LiPF<sub>6</sub> in mixed carbonate solvent (EC/DEC = 3/7, v/v). Charging and discharging control was carried out using a BLS, Tabai Espec automatic battery measurement system at a controlled temperature.

Self-discharge tests were carried out using the following method. After coin cells were charged at 1 C constant current up to 4.5 V, they were left at open circuit state for various periods and then discharged at 0.2 C down to 2.6 V. By comparing the charging and discharging capacities, we calculated their self-discharge rate. We charged them continuously at 1 C until they were at 4.5 V again and then discharged them at 0.2 C down to 2.6 V without a break. We evaluated their recovery rate based on the discharge capacities values with and without breaks.

### 3. Results and discussion

Fig. 1 is a surface image of a PTMA–carbon composite electrode. PTMA particles several 10 of microns in diameter are buried under the carbon fiber, and there are many void spaces in the electrode surface. The deposited density of the electrode was 0.4–0.5 g cm<sup>-3</sup>.

A cyclic voltammogram of the PTMA–carbon composite electrode is shown in Fig. 2. A sharp singlet redox couple was observed and the standard redox potential was found to be 3.58 V versus Li/Li<sup>+</sup>. The scan speed was 1 mV s<sup>-1</sup>, and the peak range was 0.3 V. That means it took only 300 s to completely oxidize

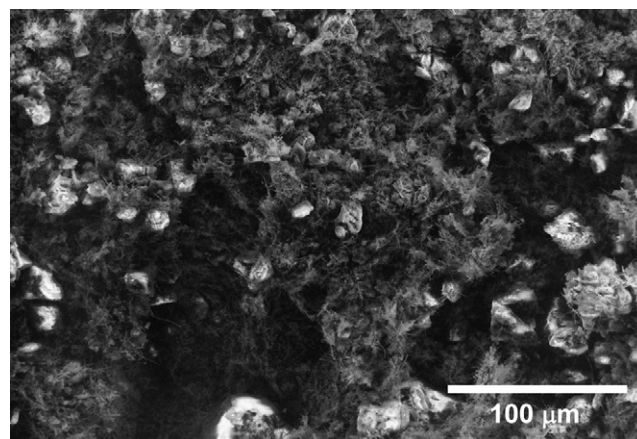


Fig. 1. Scanning electron microscope (SEM) image of a PTMA–carbon composite electrode made from a water-based slurry.

the electrode. In spite of this rapid oxidation speed, peak separation was quite small, indicating rapid charge transfer. The area under the oxidation peak was almost equal to that under the reduction peak, indicating excellent redox efficiency. Compared with previous reports, the peak height to background ratio increased considerably because of the improved homogeneity of the active material.

A Li/PTMA half-cell was fabricated after filling the voids of the electrode with liquid electrolyte. The charging and discharging curves obtained at 45 °C and 2.6–4.5 V are shown in Fig. 3. The charging and discharging current was set to 0.3 mA, which corresponds roughly to the 1 C rate. An obvious plateau is seen for both the charge and discharge processes. The average discharge voltage was 3.51 V. Previous reports indicated that the specific capacity of PTMA was 70–80 mAh g<sup>-1</sup>, but this electrode yielded 110 mAh g<sup>-1</sup>. This value corresponds roughly to that of the theoretical capacity (111 mAh g<sup>-1</sup>) calculated from the hypothesis that all radical units contribute to a one-electron reaction.

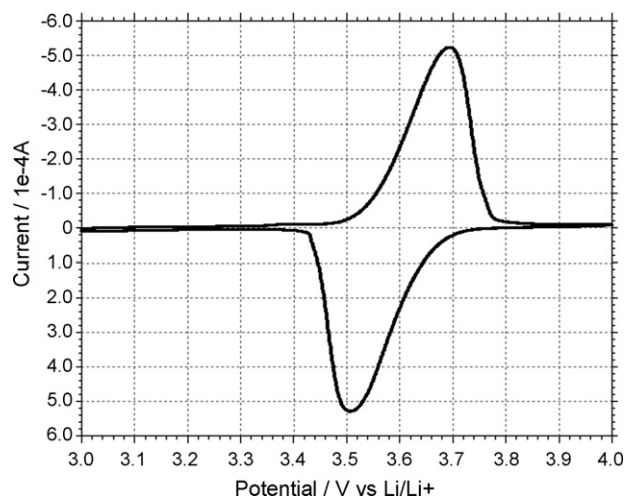


Fig. 2. Cyclic voltammogram of a PTMA–carbon composite electrode made from a water-based slurry in EC/DEC = 3/7, 1 M LiPF<sub>6</sub> electrolyte.

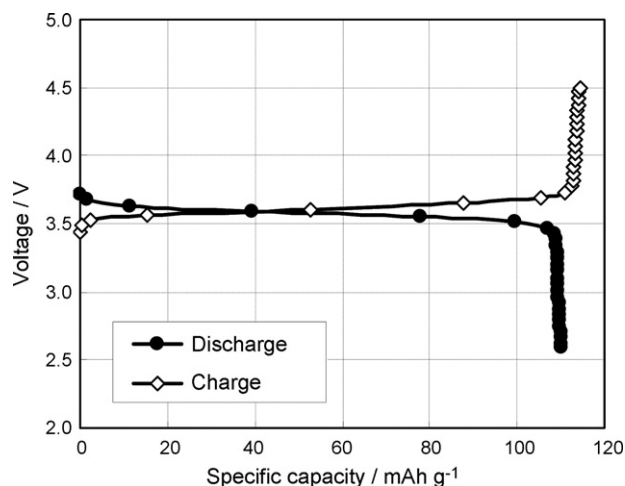


Fig. 3. Charge and discharge curves for a Li/PTMA half-cell (45 °C, 2.6–4.5 V). Charging and discharging current was set to 0.3 mA, which corresponds roughly to the 1 C rate.

The cycling performances of Li/PTMA half cells at 20, 45, and 60 °C are shown in Fig. 4. When cycling was carried out between 2.6 and 4.5 V at 20 °C, the capacity decreased gradually. However, 92% of the initial capacity was maintained after 100 cycles. This cycling stability was not as good as that reported for other Li/PTMA half cells. It was previously reported that 98% of initial capacity was retained after 500 cycles [3]. We suspected that the PTMA cathode described here retained a considerable amount of water from the water slurry fabricating process. Higher temperatures were also found to degrade capacity faster. After 100 cycles at 45 °C, only 15% of the initial capacity was lost, while at 60 °C, 50% was lost. Side reactions, such as decomposition of the electrolyte or inactivation of the lithium anode surface caused by moisture, might be accelerated by elevated temperatures.

The 1 and 5 C cycling rates at 20 °C are shown in Fig. 5. The charging rates were set to be the same as the discharging rates. A slightly larger degradation of capacity was seen at the 5 C than at the 1 C cycling rate. We think that increased impedance during

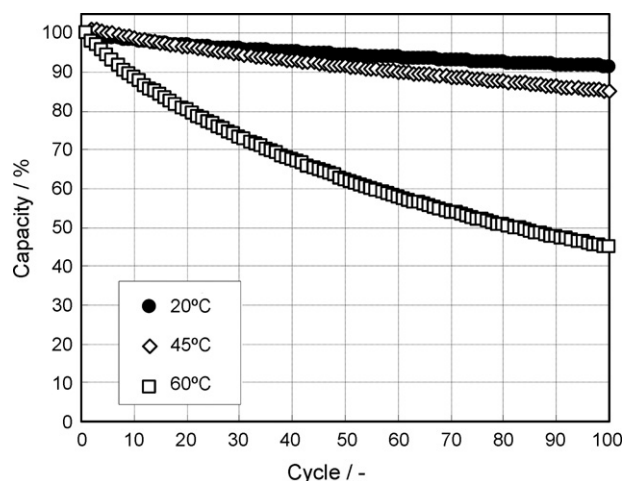


Fig. 4. Temperature dependence (20, 45 and 60 °C) of cycling performance (2.6–4.5 V) of a Li/PTMA half-cell at the 1 C rate.

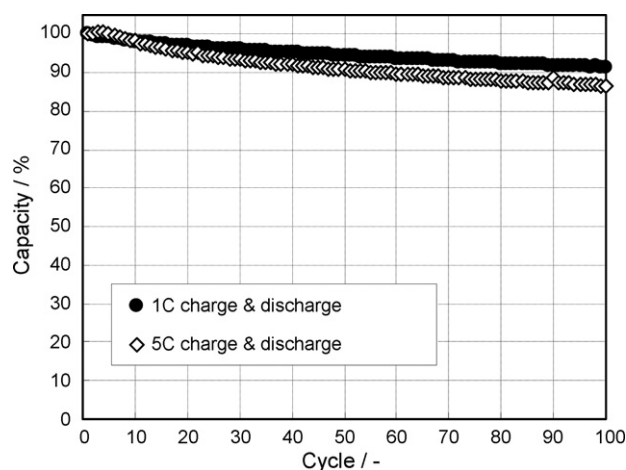


Fig. 5. Cycling performance of a Li/PTMA half-cell at 1 and 5 C rates.

cycling may have caused the charging capacity degradation at the higher rate. We concluded that the degradation caused by repeated cycling was more serious than that caused by ageing.

The rate dependences of the discharge curves in the range from 0.5 to 20 C at 20 and 45 °C are shown in Fig. 6. All charging processes were carried out at the 1 C rate. We found that the higher discharge rate caused a decrease in the voltage during discharge and a degradation of the capacity. Because the voltage drop was directly proportional to the discharge rate, the voltage drop is attributed mainly to the ionic resistance of the electrolyte. Therefore, the results obtained at 20 °C showed a comparatively smaller decrease in discharge voltage than those at 45 °C.

In contrast to the above results, the capacity degradation observed at 20 °C was similar to that at 45 °C. It appears that the degradation of discharge capacity is related to low efficiency rather than electrode resistance. We suspect that the central part of the PTMA particles was not contributing to the discharge process at high discharge rates, because there were too few reactant ions whose motion is dominated by the diffusion process. However, even at the high discharge rate of 20 C, the observed capacity was more than 70% of that at the 1 C rate. This indicates that the Li/PTMA half-cell has promise as a high specific power energy source.

The self-discharge rate of these cells at 20 °C is shown in Fig. 7. A high rate of self-discharge was observed and was found to be proportional to the square root of elapsed time. After 1 week of storage, 38% of the capacity had disappeared, but was recovered well (>98.5%) in the next cycle. This indicates that the material itself was not damaged by storage. We think that self-discharge is caused by the redox shuttle mechanism. PTMA dissolved in the electrolyte might operate as a redox shuttle species. In this case, strong chemical bonding in the electrode and further purification of the PTMA may be effective in decreasing the self-discharge rate.

A graphite anode was prepared for use in a coin cell with a PTMA cathode. The first charging capacity of the anode was adjusted to be same as that of the PTMA cathode with the value of 0.30–0.35 mAh. Fig. 8 shows an example of the first charge and discharge curves of a Li/graphite half-cell. The first charge and

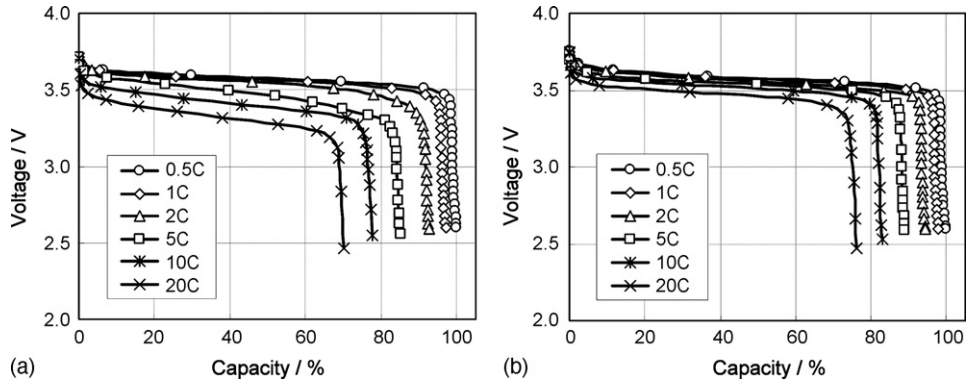


Fig. 6. Discharge rate capabilities of a Li/PTMA half-cell at (a) 20 °C and (b) 45 °C.

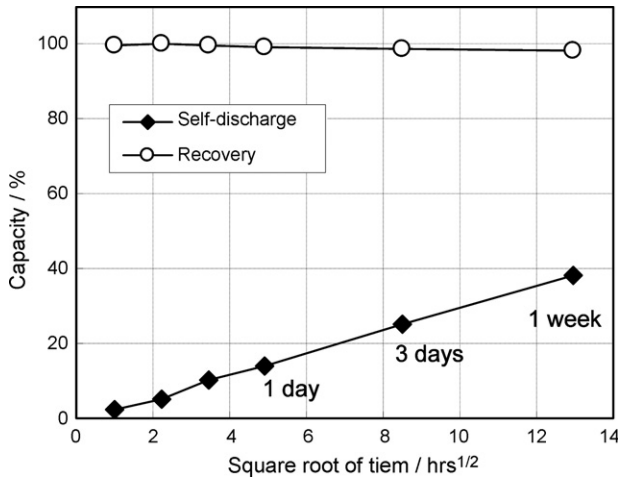


Fig. 7. Self-discharge rate of a Li/PTMA half-cell at 20 °C.

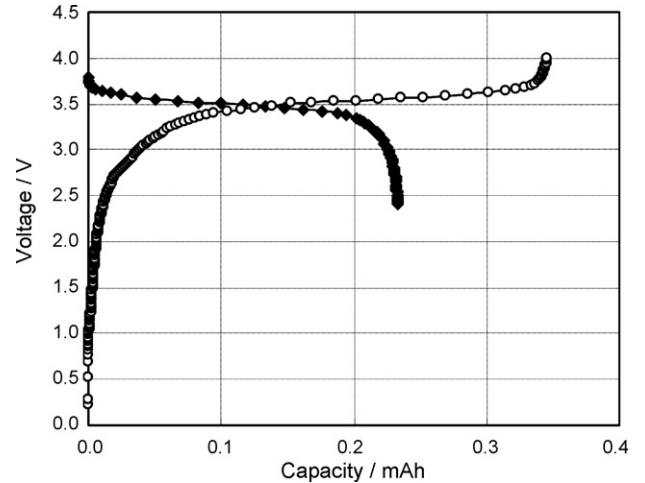


Fig. 9. First charge and discharge curves of graphite/PTMA cell at 20 °C. Charging and discharging current was 0.1 mA.

discharge capacities were 0.34 and 0.26 mAh, respectively, indicating that 24% of the initial charging capacity was irreversible. The average voltage was 0.15–0.20 V.

Fig. 9 shows the first charging and discharging curves for a graphite/PTMA cell. The first charge and discharge was carried out at a constant current of 0.1 mA, corresponding roughly

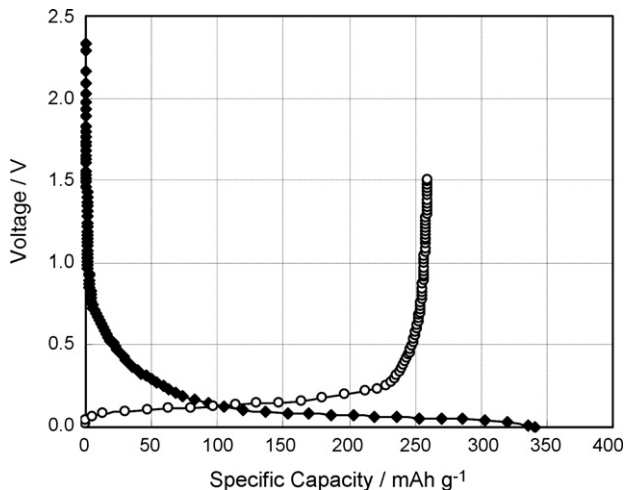


Fig. 8. First charge and discharge curves of a Li/graphite half-cell at 20 °C.

to the 1/3 C rate of first charge capacity. The upper and lower voltage limits were 4.0 and 2.6 V, respectively. Though the open circuit voltage of the as-prepared cell was about 0.2 V, the voltage increased gradually while charging. The charging voltage plateau was at 3.5 V, and the voltage rose suddenly after the plateau. The first charging capacity was 0.35 mAh, and the average voltage was 3.4 V. The first discharge curve also had a good shape. The discharge voltage plateau was at 3.5 V, and the capacity was 0.23 mAh. This means that 0.11 mAh (33%) of the first charge capacity was irreversible. As described above, the graphite anode itself had 24% irreversible capacity, so this percentage increased as a result of assembling a complete cell. The small MCMC graphite particle (3 μm) used for this experiment is the main reason for such a large capacity loss. If we used a PTMA cathode, as reported elsewhere [3], the salt (LiPF<sub>6</sub>) concentration in the electrolyte solution would change continuously during the charging and discharging processes. In the completely discharged state (DOD = 100%), the concentration was set to 1.0 M, but in the charged state, it would be lower than 1.0 M. Therefore, we think there is a possibility that the change of salt concentration during charging affected the component of solid electrolyte interface (SEI) layer on graphite. That might have caused an increase in the irreversible capacity.

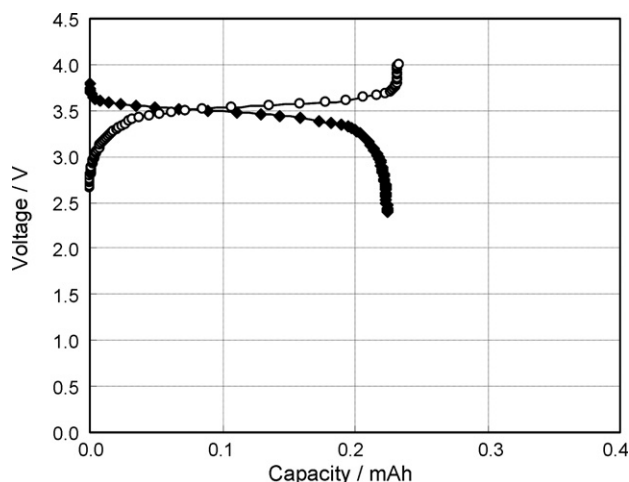


Fig. 10. Second charge and discharge curves of graphite/PTMA half-cell at 20°C. Charging and discharging current was 0.2 mA.

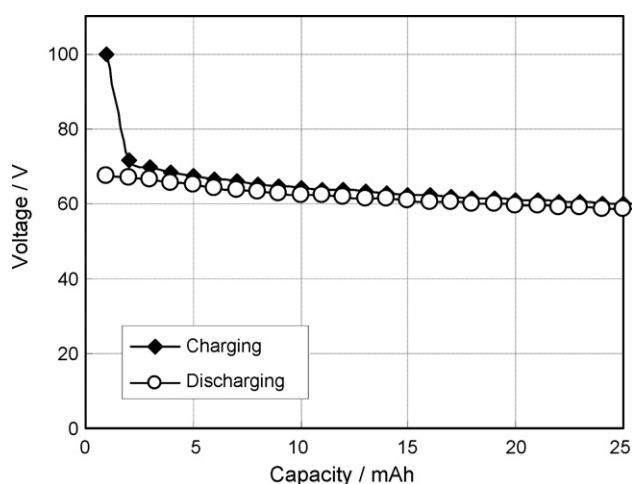


Fig. 11. Cycling performance of graphite/PTMA half-cell at 20°C. Charging and discharging current was 0.2 mA.

Fig. 10 shows the second charge and discharge curves. Charging and discharging were carried out at a constant current of 0.2 mA, corresponding to the 1.1 C rate. The upper and lower voltage limits were 4.0 and 2.6 V, respectively. We found that the graphite/PTMA cell stabilized after the second cycle. The charge and discharge voltage plateaus were observed around 3.5 V and their capacities were 0.23 and 0.22 mAh, respectively.

Cycling behavior is shown in Fig. 11. The cycle was repeated at a constant current of 0.2 mA between 2.6 and 4.0 V. The

discharge capacity decreased gradually, and at the 25th cycle, 87% of the initial capacity was obtained. Although a large irreversible capacity was observed during the first cycle, it almost disappeared after that. After the 10th cycle, Coulombic efficiency reached 97% and continued to improve during additional cycling.

#### 4. Conclusion

We used a water-based slurry to prepare PTMA composite electrodes, and succeeded in making homogeneous electrodes. The utilization of active material was better than in previous work and almost equaled the theoretical specific capacity ( $111 \text{ mAh g}^{-1}$ ). Lithium half-cells using these PTMA electrodes were fabricated, and the cycling performance, temperature dependence, rate capability, and self-discharge rate were measured in detail. Although there are problems in cycling stability at high temperature and self-discharge, these cells showed good rate capability. Because the full cells were assembled with graphite anodes, they showed a first-cycle irreversible capacity of 24%. The capacity stabilized after the second cycle, which is a promising result from the viewpoint of applying the PTMA electrodes practically.

#### Acknowledgements

This work was partially supported by a NEDO project to develop a high-power density organic radical battery for data-backup. It was also partially supported by the Department of Energy and NEC Corporation under agreement no. LB05-001485. We are grateful to Prof. Hiroyuki Nishide (Waseda University), Ms. Yukiko Morioka, Dr. Etsuo Hasegawa, Mr. Masato Shirakata, and Dr. Yoshimi Kubo (NEC) for fruitful discussions.

#### References

- [1] F. MacCorquodale, J.A. Crayston, J.C. Walton, D.J. Worsfold, *Tetrahedron Lett.* 31 (1990) 771.
- [2] H. Nishide, S. Iwasa, Y.J. Pu, T. Suga, K. Nakahara, M. Satoh, *Electrochim. Acta* 50 (2004) 827.
- [3] K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, E. Hasegawa, *Chem. Phys. Lett.* 359 (2002) 351.
- [4] J. Iriyama, K. Nakahara, S. Iwasa, Y. Morioka, M. Suguro, M. Satoh, *IEICE Trans. E85-C* 6 (2002) 1256.
- [5] M. Satoh, K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, *IEICE Trans. E87-C* 12 (2004) 2076.