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Practical performances of Li-ion polymer batteries with $LiNi_{0.8}Co_{0.2}O_2$, MCMB, and PAN-based gel electrolyte

Hiroyuki Akashi*, Mashio Shibuya, Ken Orui, Gorou Shibamoto, Koji Sekai

Sony Corporation, Yokohama Research Center, Hodogaya-ku, Yokohama 240-0036, Japan

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Abstract

The practical performances and thermal stability of Li-ion polymer batteries with $LiNi_{0.8}Co_{0.2}O_2$, mesocarbon microbead-based graphite, and poly(acrylonitrile) (PAN)-based gel electrolytes are reported. The gel electrolyte, which shows a fire-retardance by itself as well as good chemical stability effectively improved thermal stability of the Li-ion polymer battery up to 170 °C. We also found that the mesocarbon microbead-based graphite showed better coulombic efficiency even though the gel electrolyte contained PC and GBL. An evaluation of cell performances showed that the electrodes and the gel electrolyte were promising material for a next-generation Li-ion polymer battery.

Keywords: Li-ion polymer battery; Gel electrolyte; Poly(acrylonitrile); Thermal stability; Lithium nickel dioxide; Mesocarbon microbeads

1. Introduction

Li polymer batteries using gel electrolytes are currently attracting much attention since they have both high energy density and reliability [1–3].

There has been extensive research on the physical and electrochemical properties of gel electrolytes [4–25] but comparatively little research on practical polymer batteries using gel electrolytes [26–35]. The combination of a gel electrolyte and electrode-active materials greatly affects cell performance no less than ionic conductivity and the potential window of the gel electrolyte does. Thus, further research on the cell design, such as optimization ofc electroactive materials, the gellation process, and capacity cbalance for high performance Li-ion polymer battery is required.

We recently reported that poly(acrylonitrile) (PAN)-based gel electrolyte has good fire-retardance, which ensures the reliability of the Li polymer battery even though the organic electrolyte solution is immersed in the gel electrolyte [15,16,36]. We previously reported that a 3V-class Li primary cell with PAN-based gel electrolyte exhibited excellent cell performance in practical use [34].

$LiNiO_2$ is expected to be a next-generation positive-electrode material because this material shows higher capacity than $LiCoO_2$. However, $LiNiO_2$ is thermally less stable than $LiCoO_2$ so research continues to improve the thermal stability [37,38].

We report here advantages of using the PAN-based gel electrolyte to improve the thermal stability and practical cell performances of the Li-ion polymer battery with $LiNi_{0.8}Co_{0.2}O_2$.

2. Experimental

The positive electrode was prepared by combining 3 wt.% of PVdF and 6 wt.% of JSP (graphite, Nihon Kokuen) with $LiNi_{0.8}Co_{0.2}O_2$. The negative electrode was prepared by combining 9 wt.% of PVdF with Mesocarbon microbead-based graphite (MCMB6-28, Osaka Gas Chemical). The positive electrode and negative electrode were coated on aluminum foil and copper foil, respectively. A porous membrane made of poly(propylene) (PP, Celguard 3401) was used for the separator material.

The gel electrolyte consisted of ethylene carbonate (EC, lithium-battery grade, Mitsubishi), propylene carbonate (PC, lithium-battery grade, Mitsubishi), γ-buthyrolactone (GBL, lithium-battery grade, Mitsubishi), poly(acrylonitrile) ($M_w = 1.5 \times 10^4$, Polyscience Inc.), and lithium hexafluorophoshate ($LiPF_6$, Tomiyama). The PAN was dried under vacuum at 80 °C for 24 h before use. EC, PC, GBL, and

* Corresponding author. Present address: Energy R&D Department, Energy Company, Core Technology and Network Company, Sony Corporation, Atsugi Technology Center No. 2, 4-16-1 Okada, Atsugi-shi, Kanagawa 243-0021, Japan. Tel.: +81-46-227-2342; fax: +81-46-227-2222.
E-mail address: hiroyuki.akashi@jp.sony.com (H. Akashi).

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$LiPF_6$ were used as received. Gel electrolytes were synthesized as described previously [34]. The component ratio of the gel electrolytes was PAN/EC/PC/GBL/$LiPF_6$ = 12/44/22/15/7 (in mol%).

The gel electrolyte was coated on both electrodes by a sol-casting process before stacking the separators between positive and negative electrodes. The hot sol solution of the PAN-based gel electrolyte was coated by a doctor blade in order to penetrate the solution into deep cavities of the porous electrodes sufficiently. Then, these electrodes were stacked together before the sol solution transformed to the gel electrolyte. The sol solution in the stacked electrodes was transformed without any additives for the cross-linking reaction around at 40 °C. Li-ion polymer batteries were fabricated by packing the stacked electrodes and separators in a laminated flexible film. In order to avoid moisture, Al and Cu meshes were used as current collectors for the positive and negative electrodes, respectively. All fabrication work took place in a dry room with a dew point not lower than −40 °C.

The half-cell performance of the negative electrode was measured using 2016 coin cells. The battery and the cell performance was evaluated using commercial test equipment (TOSCAT 3000, Toyo system Inc.).

The degree of electrochemical stability of the gel electrolyte was determined using cyclic voltammetry. A working electrode, a counter electrode, and a reference electrode were used for Ni, Li, and Li, respectively. The scanning rate was 5 mV/s.

3. Results and discussion

3.1. Electrochemical stability of the PAN-based gel electrolytes

Typical CV profiles of the PAN-based gel electrolyte in the range from 2.5 to 5.0 V (versus Li/Li^+) and −0.30 to 1.0 V (versus Li/Li^+) are shown in Figs. 1 and 2, respectively. The background current was less than 20 μA/cm^2, and no significant decomposition current was observed in the former profile. Faradaic current in the latter profile showed good cycleability during the Li-plating and stripping reaction. These results indicate that the gel electrolyte has a potential window wide enough for using in a Li-ion battery.

3.2. Coulombic efficiency of graphite with the gel electrolyte

Fig. 3 shows initial charge and discharge profiles for different graphite/Li-half cells with a PAN-based gel electrolyte, respectively. Both PC and GBL caused degradation of coulombic efficiency during Li^+ intercalation for conventional graphite material (sample A). The efficiency was less than 69%. It is well known that the coulombic efficiency of a negative electrode reaction with graphite material is seriously degraded by PC and/or GBL in the electrolyte solution [39–42].

On the contrary, MCMB achieved good coulombic efficiency, reaching more than 87%, while the composition of the PAN-based gel electrolyte was the same.

The difference in the charge profiles in the range from 1.0 to 0.05 V indicates that the reduction of PC and/or GBL was effectively restrained by using MCMB while the charge reaction proceeded. Some physical properties of the graphites were shown in Table 1. Slight differences could be seen in the bulk properties between the two graphites. Therefore, the differences might be caused by a difference in a sort of morphologic feature on its surface of the MCMB. Further investigation about this phenomenon is under going.

3.3. Cell performances of the Li-ion polymer batteries

Fig. 4 shows typical charge and discharge profiles of a Li-ion polymer battery. The average discharge voltage reached

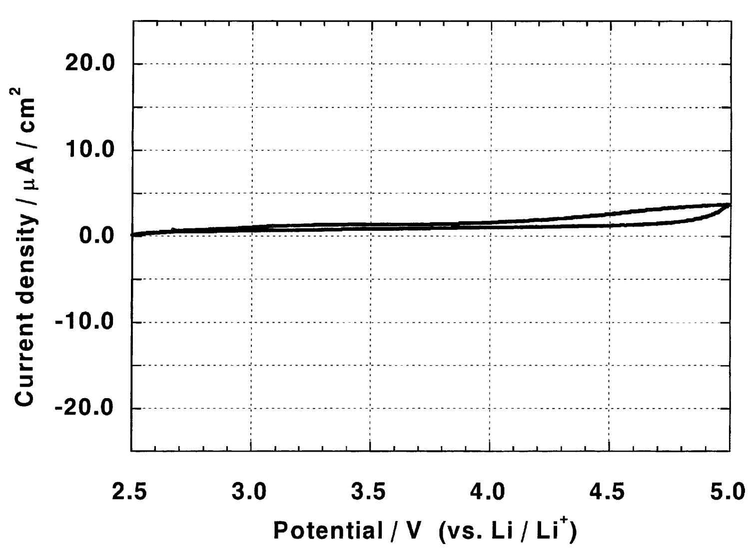

Fig. 1. CV profile of the PAN-based gel electrolyte. W/C/R = Ni/Li/Li, scan rate 5 mV/s.

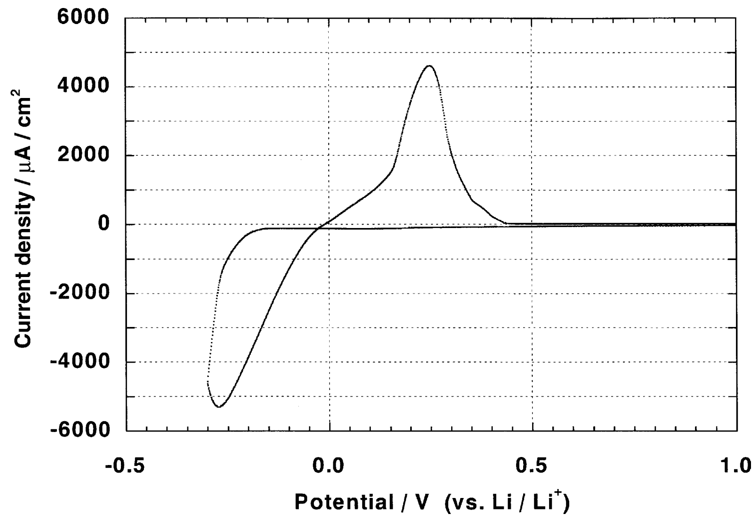

Fig. 2. The plating and stripping behavior of Li for the PAN-based gel electrolyte. W/C/R = Ni/Li/Li, scan rate 5 mV/s.

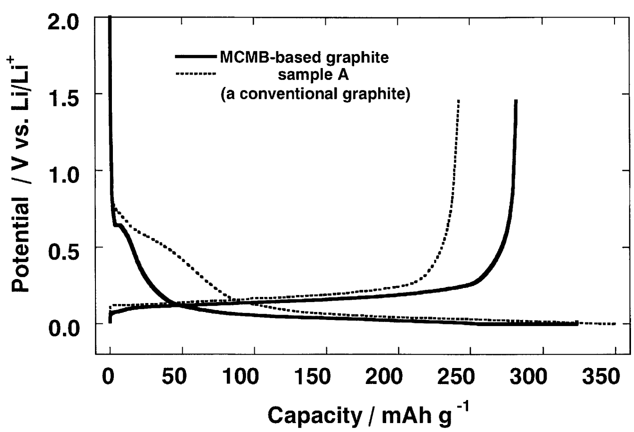

Fig. 3. The comparison of the initial charge and discharge profiles with the MCMB-based graphite and a conventional graphite (sample A). Charge and discharge current 1 mA, constant current voltage 0 V, cut-off voltage 2.0 V.

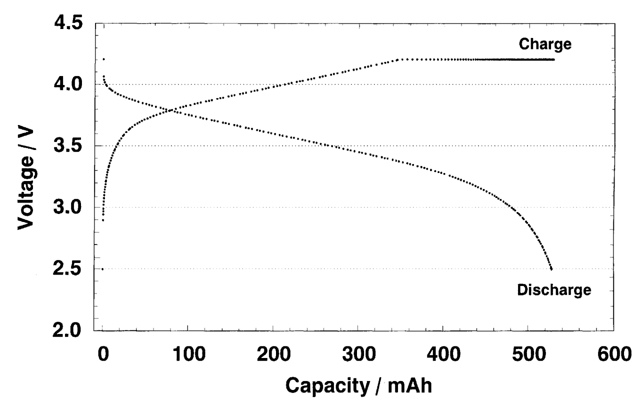

Fig. 4. Typical charge and discharge profile of the Li-ion polymer battery with $LiNi_{0.8}Co_{0.2}O_2$, MCMB, and a PAN-based gel electrolyte. Nominal capacity 550 mAh (on average), charge and discharge current 0.5 C, constant current voltage 4.2 V, cut-off voltage 2.5 V.

3.5 V at 0.2 C. MCMB-based graphite for the negative electrode material improved initial coulombic efficiency to 87%. The utilization of the $LiNi_{0.8}Co_{0.2}O_2$ with the PAN-based gel electrolyte was estimated to be almost 100% when the initial charge capacity was assumed to be 175 mAh/g at 0.2 C. The utilization was determined by Eq. (1) as follows:

$$\text{utilization}\,(\%) = \frac{C_{\text{PAN}}}{C_{\text{EC and DMC}}} \tag{1}$$

where C_{PAN} is the charge capacity with the PAN-based gel electrolyte and $C_{\text{EC and DMC}}$ the charge capacity with a EC and DMC-based liquid electrolyte.

Table 1
Physical properties for MCMB6-28 and sample A

Properties	MCMB6-28	Sample A
Specific surface area (m^2/g)	3.6	3.8
True density (g/cm^3)	2.20	2.27
d_{002} (nm)	0.34	0.34

The EC and DMC-based liquid electrolyte was consisted of a mixed solvents of EC (50 vol.%) and DMC (50 vol.%) with 1 M $LiPF_6$.

Fig. 5 shows the typical drain performance of a Li-ion polymer battery. The capacity retention ratio reached to 94.1, 87.5, and 77.1% at 0.65, 1.3, and 2.2 C, respectively. The observed drain performance of the Li-ion polymer batteries was excellent as high as that of some commercialized Li-ion batteries with a liquid electrolyte solution.

Fig. 6 shows the typical cycle performance of a Li-ion polymer battery. The capacity retention ratios were 93.9% and 85.2% at the 100th and the 400th cycle, respectively. This performance indicates that reversibility of the electrode reactions on the positive electrode and negative electrode is quite stable even at a practical current condition of 0.5 C. We also found that GBL did not cause degradation in a cycle performance of the polymer battery because the PAN-based

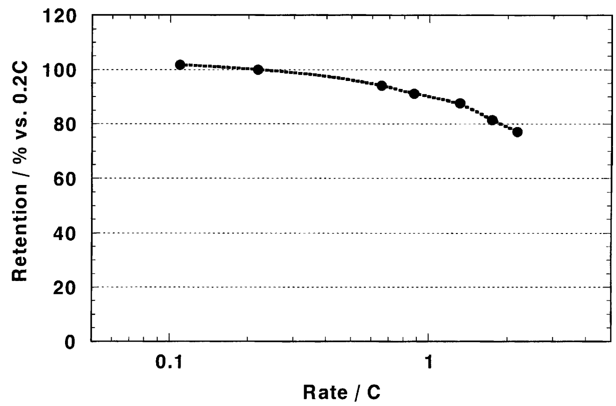

Fig. 5. Relation between load current and capacity of the Li-ion polymer battery with $LiNi_{0.8}Co_{0.2}O_2$, MCMB, and a PAN-based gel electrolyte. The capacity retention ratios at various discharge rate were estimated by the capacity at 0.2 C.

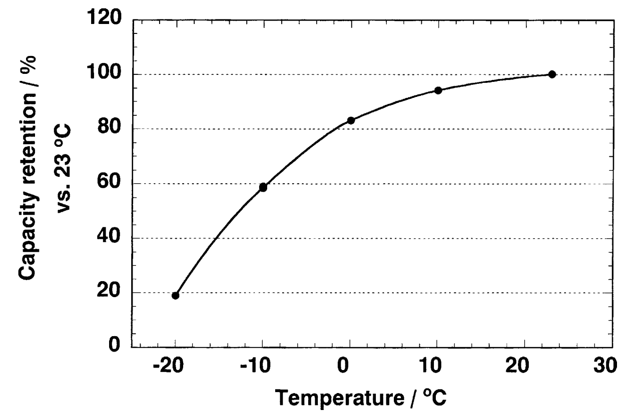

Fig. 7. Relation between cell temperature and capacity of the Li-ion polymer battery with $LiNi_{0.8}Co_{0.2}O_2$, MCMB, and a PAN-based gel electrolyte. Nominal capacity 550 mAh, charge and discharge current 0.5 C, constant current voltage 4.2 V, cut-off voltage 3.0 V. The capacity retention ratio was estimated by the capacity at 23 °C.

gel electrolyte without GBL provided the similar capacity fading ratio.

The discharge capacity of a Li-ion polymer battery is plotted against different operation temperature in Fig. 7. Despite the load current was relatively high, the retention ratio of discharge capacity at 23 °C reached 82, 58, and 19% at 0, −10, and −20 °C, respectively.

Fig. 8 shows how operation temperature influences on capacity degradation of the Li-ion polymer batteries. No significant degradation on discharge capacity was observed under the experimental condition.

Capacity degradation after a hot-storage test was also investigated. The batteries with 100% state of charge (SOC) had been stored at 60 °C for 15 h, after which monitoring of the capacity was resumed at 23 °C. The tendency of the capacity degradation seems to be not affected by the hot-storage test, as is shown in Fig. 9.

This result indicates that the PAN-based gel electrolyte contributed to improving the electrochemical stability of the Li-ion polymer battery.

The cell performance of the Li-ion polymer battery also suggested the importance of an electrochemical interface between the gel electrolyte and the electrodes with better contact.

Because overpotential during charge and discharge reactions should be restrained as small as possible in order to maximize reaction efficiency, many attempts have been focused to improve the ionic conductivity of the gel electrolyte.

The electrochemical interface between the PAN-based gel electrolyte and the electrodes improved using both optimized materials, such as electrode, electrolyte, and separator, and the sol-casting process.

PAN-based gel electrolyte is a type of physical gel in which the cross-linking point is formed by a crystal part of the host polymer. The gellation reaction, that is the sol–gel transformation, is controlled by temperature and there need not be any additional cross-linker which often causes a coulombic efficiency loss in the charge and/or discharge reaction.

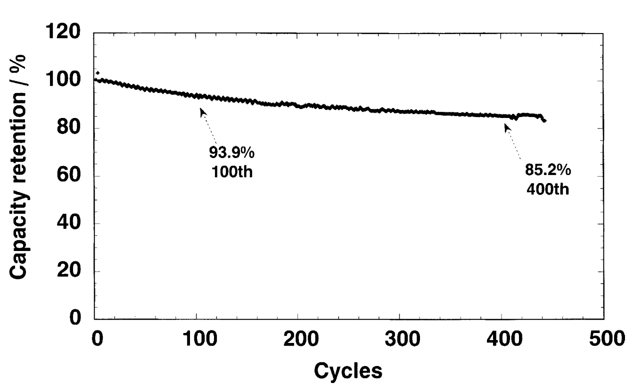

Fig. 6. Cycle performance of the Li-ion polymer battery with $LiNi_{0.8}Co_{0.2}O_2$, MCMB, and a PAN-based gel electrolyte. Nominal capacity 550 mAh, charge and discharge current 0.5 C, constant current voltage 4.2 V, cut-off voltage 3.0 V. The capacity retention ratio was estimated by the capacity at second cycle.

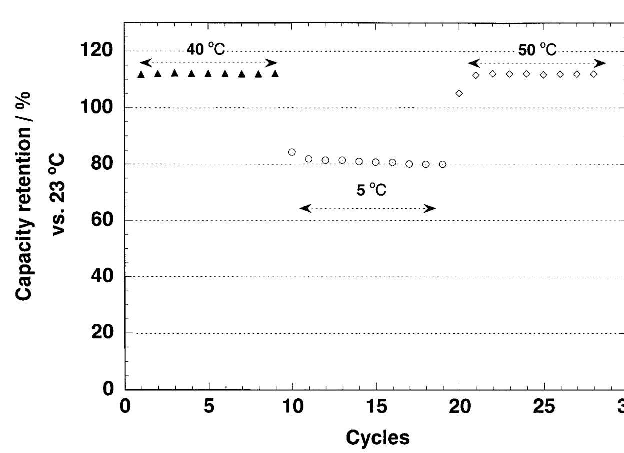

Fig. 8. Cycle performance at various cell temperature of the of the Li-ion polymer battery with $LiNi_{0.8}Co_{0.2}O_2$, MCMB, and a PAN-based gel electrolyte. Nominal capacity 550 mAh, charge and discharge current 0.5 C, constant current voltage 4.2 V, cut-off voltage 3.0 V. The capacity retention ratio was estimated by the capacity at 23 °C.

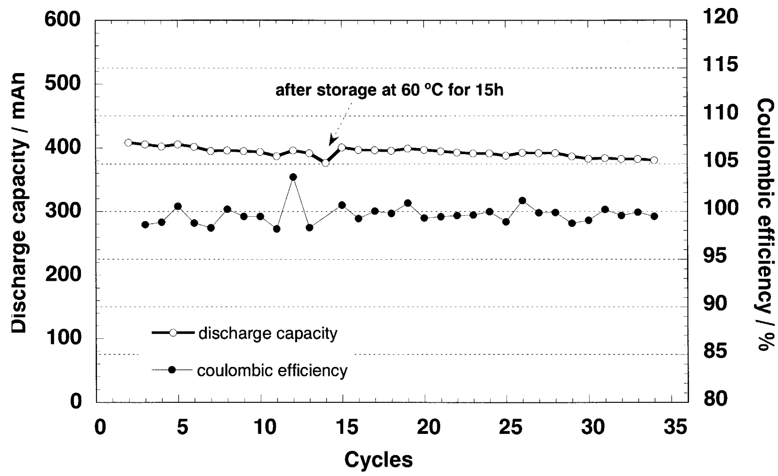

Fig. 9. The influence of the hot-storage test on the cycle performance of the Li-ion polymer battery with $LiNi_{0.8}Co_{0.2}O_2$, MCMB, and a PAN-based gel electrolyte. Nominal capacity 420 mAh (the smaller size, the energy density of the battery was the same as the others), charge and discharge current 0.5 C, constant current voltage 4.2 V, cut-off voltage 3.0 V. The capacity retention ratio was estimated by the capacity at second cycle.

Most of the porous electrode materials for Li-ion batteries have a narrow and deep cavity, thus, the sol-casting process is also a effective method for applying the PAN-based gel electrolyte to the surface of an electrode-active material. A sol electrolyte penetrates more easily to the cavity of the electrode material so a good electrochemical interface can be formed by transforming the sol electrolyte to a gel electrolyte.

Since a PAN-based gel electrolyte with electrochemical stability played the role of glue to ensure the physical contact of the electrodes at the interface, excessive overpotential was avoided and excellent cell performance was achieved.

Fig. 10 shows a typical example of the thermal stability of a Li-ion polymer battery. The battery was stable up to 172 °C in a heated chamber even though the state of charge was 100%. This result indicates that the PAN-based gel electrolyte provides high thermal stability in the electrochemical interface between the PAN-based gel electrolyte and the electrodes even then the battery is abused.

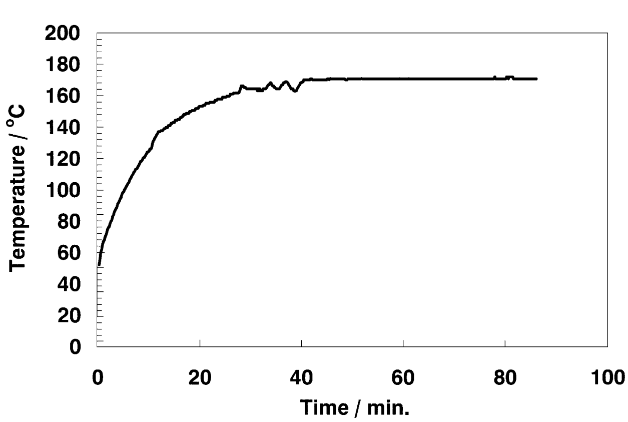

Fig. 10. Typical cell temperature profiles of the fully charged Li-ion polymer battery with $LiNi_{0.8}Co_{0.2}O_2$, MCMB, and a PAN-based gel electrolyte. Nominal capacity 550 mAh, charge current 0.5 C, constant current voltage 4.2 V.

4. Summary

We have shown that the cell performance of Li-ion polymer batteries with a fire-retardant poly(acrylonitrile)-based gel electrolyte is sufficient for practical use.

The PAN-based gel electrolyte was stable in the wide potential range from −0.25 to 5.00 V. MCMB improved initial coulombic efficiency even though the PAN-based gel electrolyte contained PC and GBL with a relatively high concentration.

Optimized sol–gel transformation of a PAN-based gel electrolyte and the sol-casting process minimized overpotential during charge and discharge reaction so better cell performance was achieved. The PAN-based gel electrolyte also provides high thermal stability for a Li-ion polymer battery with $LiNi_{0.8}Co_{0.2}O_2$. The polymer battery was stable up to 170 °C at 4.20 V.

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