Room temperature rechargeable polymer electrolyte batteries

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Abstract

Polyacrylonitrile (PAN)- and poly(vinyl chloride) (PVC)-based Li^+-conductive thin-film electrolytes have been found to be suitable in rechargeable Li and Li-ion cells. $Li/Li_xMn_2O_y$ and $carbon/LiNiO_2$ cells fabricated with these electrolytes have demonstrated rate capabilities greater than the C-rate and more than 375 full depth cycles. Two-cell $carbon/LiNiO_2$ bipolar batteries could be discharged at pulse currents as high as 50 mA/cm^2.

Keywords: Rechargeable lithium batteries

1. Introduction

Worldwide research and development efforts are currently underway to fabricate all-solid-state, rechargeable Li and Li-ion batteries utilizing Li^+-conductive polymer electrolytes [1]. Advantages of these batteries are many; for example, they can be manufactured as thin-film laminates of various shapes and sizes suitable for use in portable consumer products such as videocameras, computers, radios and cellular telephones. Remarkable progress has been made in recent years in understanding the fundamental properties of highly conductive polymer electrolytes [2] and in the fabrication of thin-film rechargeable Li batteries [3]. A significant amount of data have also been collected on the cycling of rechargeable Li cells using intercalation cathodes such as TiS_2 and V_6O_{13} [4,5]. Because of the low conductivity of the classical poly(ethylene oxide) (PEO)-based electrolytes, however, these cells are operated at elevated temperatures of 80 to 100 °C. Consequently, polymer electrolytes containing liquid plasticizers have gained wide acceptance [1,5]. These plasticizers are high dielectric constant, low vapor pressure organic molecules such as ethylene carbonate (EC). Although plasticized electrolytes lack the beauty of virgin solid polymer electrolytes, their exceptionally high ambient temperature conductivities, usually exceeding 10^{-3} Ω^{-1} cm^{-1}, and processability as thin-films, have made them attractive as novel electrolytes possessing ionic conductivity approaching that of organic liquid electrolytes and mechanical stability reminiscent of solid polymer electrolytes.

Several polymer matrices have been plasticized to obtain a conductivity of about 2×10^{-3} Ω^{-1} cm^{-1} at room temperature. These include poly(ethylene glycol)-acrylates [5], poly(ethylene oxide)s [6], poly(vinylidene fluoride) [7], polyacrylonitrile and poly(vinyl chloride). We have developed and extensively studied polymer electrolytes based on polyacrylonitrile (PAN) and poly(vinyl chloride) (PVC). Rechargeable Li and Li-ion cells have been fabricated using both PAN- and PVC-based solid electrolytes, and their performance at room temperature is reported.

2. Results and discussion

Properties of PAN- and PVC-based solid electrolytes

A variety of PAN and PVC-based solid electrolytes containing different Li salts and plasticizers have been prepared and their morphological and electrical properties have been examined. The Li salts include $LiClO_4$, $LiAsF_6$, $LiPF_6$ and $LiN(CF_3SO_2)_2$. As plasticizers, ethylene carbonate (EC), propylene carbonate (PC), γ-butyrolactone (BL), N-methylpyrrolidone (NMP) and butylene carbonate (BC) have been investigated. Homogeneous, mechanically stable, thin-film electrolytes are formed only for certain ratios of the components. Typically, these electrolytes show a room temperature conductivity of 1.5×10^{-3} Ω^{-1} cm^{-1} [1].

The temperature dependence of the conductivities of PAN- and PVC-based electrolytes are illustrated in Fig. 1. The values range from about 4×10^{-5} Ω^{-1} cm^{-1} at -40 °C to about 2×10^{-3} Ω^{-1} cm^{-1} at 20 °C. The
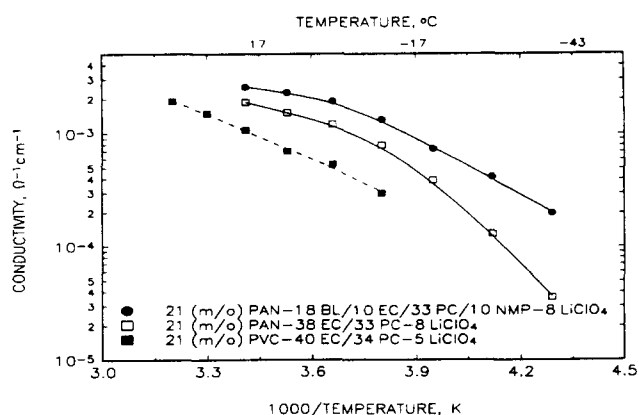
Fig. 1. Temperature dependence of the conductivities of some PAN- and PVC-based plasticized polymer electrolytes.

PAN-based electrolytes were found to be more conductive than their PVC-counterparts. The conductivity of these electrolytes can be increased, especially at subambient temperatures, by using plasticizers composed of ternary or quaternary solvent mixtures. This is illustrated in Fig. 1 by the data for the electrolytes 21 (m/o) PAN–38 EC/33 PC–8 LiClO$_4$ and 21 (m/o) PAN–18 BL/10 EC/33 PC/10 NMP–8 LiClO$_4$. At -40 °C, for example, the latter electrolyte containing a four-component plasticizer showed a conductivity of 2×10^{-4} Ω^{-1} cm^{-1}, which is about six times the conductivity of 3.5×10^{-5} Ω^{-1} cm^{-1} shown by the former electrolyte containing a plasticizer mixture of EC and PC. These results are similar to those we have obtained in non-aqueous liquid electrolytes, wherein multicomponent solvent blends have led to an increase in the electrolyte conductivity at low temperatures due, most probably, to higher mobility of Li ions in Li salt–solvates of less-ordered structures [8].

Cyclic voltammetric data revealed that the PAN- and the PVC-based electrolytes have an electrochemical stability window spanning 0.0 to 4.5 V versus Li$^+$/Li [1].

2.2. Studies of the Li/polymer electrolyte interface

To determine the stability of the Li electrode in contact with the PAN- and PVC-based polymer electrolytes, impedances of Li/polymer electrolyte/Li cells were measured as a function of storage period. The cells were of 10 cm^2 area and sealed in metallized plastic bags. To evaluate the effect of Li salts on the properties of the Li/polymer electrolyte interface, studies were also carried out with different Li salts, such as LiN(CF$_3$SO$_2$)$_2$, LiClO$_4$, LiPF$_6$ and LiAsF$_6$. ,

Fig. 2 shows the temporal evolution of the impedance of a Li/polymer electrolyte/Li cell containing the electrolyte PAN–EC/PC–LiClO$_4$ due to storage under open-circuit conditions. The impedance plots are characterized by one large semicircle at high frequencies
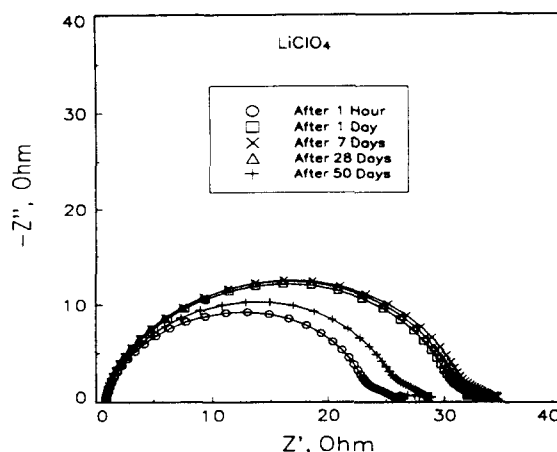

Fig. 2. Impedance plots of a Li/polymer electrolyte/Li cell as a function of storage time. The electrolyte was (in mol%) 21 PAN–38 EC/33–8 LiClO$_4$.
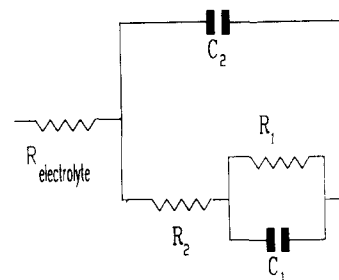

Fig. 3. Equivalent circuit for the data in Fig. 2. The calculated values for the various components are given for the impedance data obtained after a storage of 1 h. $R_1 = 227$ Ω cm^2, $R_2 = 20$ Ω cm^2, $C_1 = 4$ μF/cm^2, and $C_2 \cong 0.01$ μF/cm^2.

(> 100 Hz) and a small semicircle in the low frequency range between 1 and 100 Hz. Below 1 Hz, a portion of a spike was also discernible. In general, the data show a gradual but small increase in impedance in the course of storing the cell over a period of 50 days.

It is apparent from the impedance plots in Fig. 2 that while the diameter of the large semicircle increased as a function of time, that of the small semicircle remained almost unchanged. The former can be attributed to the growth of a passivating film on the Li surface and the latter to the charge/transfer resistance across the double layer. The data can be modelled using the equivalent circuit given in Fig. 3. Here, R_1 (the radius of the large semicircle) is the resistance due to the passivating layer and C_1 is the capacitance associated with it, and R_2 is the charge/transfer resistance and C_2 is the double-layer capacitance. Typical values for these parameters calculated from the impedance plot after storage for 1 h, given in Fig. 3, are very much similar to those obtained for Li stored in non-aqueous liquid electrolytes [9].

A summary of the impedance data for PAN-based electrolytes containing the Li salts LiClO$_4$, LiAsF$_6$, LiN(CF$_3$SO$_2$)$_2$ and LiPF$_6$ is given in Fig. 4. Data for the cell containing the LiPF$_6$-based electrolyte due to
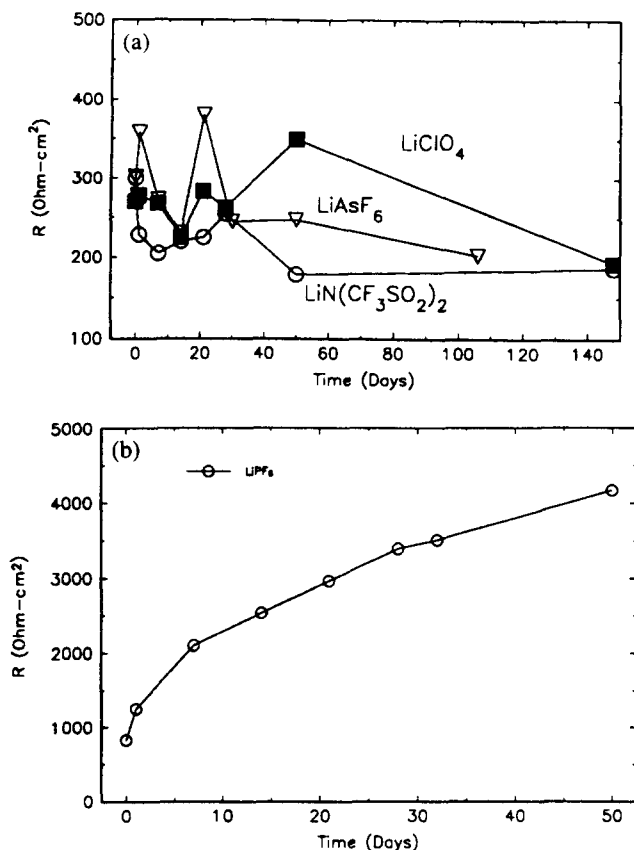
Fig. 4. Impedance data for Li/PAN-based electrolyte/Li cells as a function of storage time with different Li salts; (a) for electrolytes containing $LiClO_4$, $LiN(CF_3SO_2)_2$ and $LiAsF_6$, and (b) for $LiPF_6$.
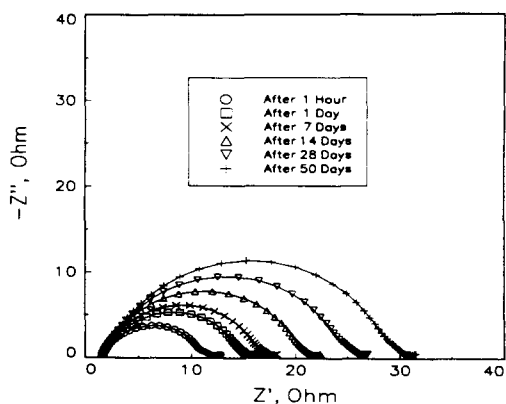

Fig. 5. Impedance plots of a Li/polymer electrolyte/Li cell as a function of storage time. The polymer electrolyte had the composition of 25 (m/o) PVC-35EC/20PC/18 triglyme-2 $LiN(CF_3SO_2)_2$.
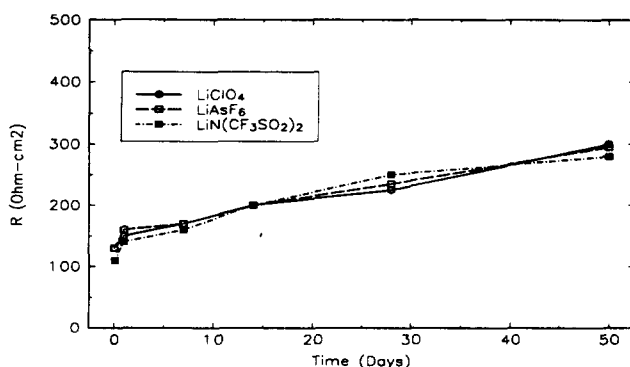

Fig. 6. Impedance data for Li/PVC-based electrolyte/Li cells as a function of storage time.

its significantly higher impedance have been placed on a scale different from that for the other Li salts (Fig. 4(b)). It is apparent from the data that the cells containing $LiPF_6$ show the highest as well as the fastest rate of increase of impedance. This indicates a high rate of reaction of this electrolyte with Li. It is possible that some $LiPF_6$ disproportionates into PF_5 and LiF during the preparation of the PAN-based electrolytes at 135 °C. The PF_5 being acidic attacks Li, causing a rise in the interfacial impedance. Among the other electrolytes, that containing $LiN(CF_3SO_2)_2$ appears to show the lowest impedance which, however, is not significantly different from those of electrolytes containing $LiClO_4$ and $LiAsF_6$.

We note in Fig. 4(a) the time-dependent fluctuations in the impedance of cells containing PAN-based electrolytes. The origin of this behavior is not understood at this time. We speculate that this might be due to fluctuations in temperature and/or a dissolution/deposition process of the passivating film present on the Li electrode.

Li/polymer electrolyte interfacial impedance data were also obtained with the PVC-based electrolytes. The impedance plots given in Fig. 5 are again characterized by a large semicircle at frequencies higher

than 50 Hz and a small, poorly resolved semicircle at low frequencies. There is a twofold increase in impedance during the course of storing the cells for 50 days. As before, the large and the small semicircles can be ascribed to the passivating film on the Li electrode and to the charge/transfer process across the Li/polymer electrolyte interface, respectively. Analysis of these data using the equivalent circuit in Fig. 3 yields $R_1 = 90$ Ω cm², $C_1 = 5$ μF/cm², $R_2 = 18$ Ω cm² and $C_2 \cong 0.01$ μF/cm². These values are slightly lower than those obtained with the PAN-based electrolytes.

Impedance data obtained with PVC-based electrolytes containing the three Li salts, $LiClO_4$, $LiN(CF_3SO_2)_2$ and $LiAsF_6$, were not significantly different from each other (Fig. 6).

2.3. Performance of rechargeable Li cells

Thin-film, rechargeable Li cells of either 10 or 50 cm² area were fabricated with both PAN- and PVC-based solid electrolytes. The cathode was the 3 V $LiMn_2O_4$, designated as $Li_xMn_2O_y$ ($x = 0.8$ and $y = 3.5$–4.0). The reversible cell reactions are depicted in Eq. (1):

$$\text{Li} + \text{Li}_x\text{Mn}_2\text{O}_y \rightleftharpoons \text{Li}_{1+x}\text{Mn}_2\text{O}_y \qquad (1)$$
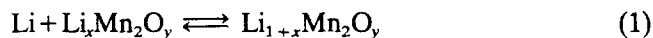
Very good rate capability and rechargeability have been realized from cells containing both types of electrolytes. For example, at 10 mA discharge current (0.2 mA/cm² or approximately $C/8$ rate), the 50 cm² cell in Fig. 7 delivered about 90% of the theoretical cathode capacity at a load voltage of 3.0 V. At 50 mA (1.0 mA cm⁻² or approximately $C/1.5$ rate), the cell delivered >50% of the full capacity at an average load voltage of 2.4 V.

Data for the continuous cycling of a 50 cm² Li/ Li$_x$Mn$_2$O$_y$ cell at 0.1 mA/cm² are given in Fig. 8. The cell has been cycled 85 times to full depths-of-discharge, at the end of which its capacity was more than 73% of the initial discharge capacity. The figure-of-merit for the cycling of the Li electrode up to the 85th cycle was 7.5.

The discharge/charge behavior of a Li/Li$_x$Mn$_2$O$_y$ cell containing a PVC-based electrolyte is shown in Fig. 9. As the data indicate, the capacity remained stable up to about 160 cycles; thereafter, it faded rapidly due most probably to the exhaustion of the Li electrode. This was confirmed by post-test analyses which showed the Li electrode to have a highly porous and mud-like
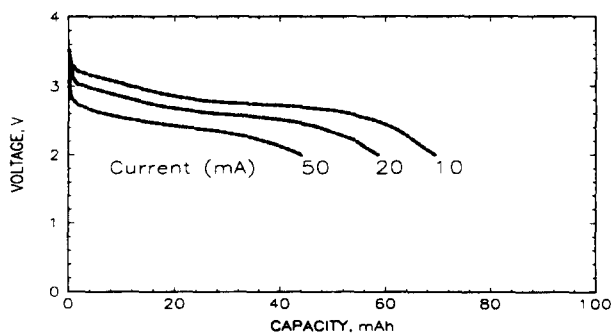

Fig. 9. Discharge/charge cycles of a 10 cm² Li/Li$_x$Mn$_2$O$_y$ cell containing a PVC-based polymer electrolyte. The Li to cathode capacity ratio was 12.5.

Fig. 7. Capacity–rate behavior of a 50 cm² Li/Li$_x$Mn$_2$O$_y$ cell containing a PAN-based electrolyte.
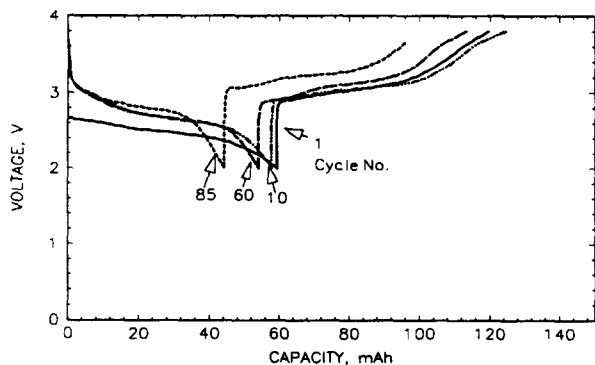

Fig. 8. Cycling performance of a 50 cm² Li/Li$_x$Mn$_2$O$_y$ cell containing a PAN-based polymer electrolyte. The cell was cycled at 0.1 mA/ cm² between 2.0 and 3.8 V. The Li to cathode capacity ratio was 8.5.
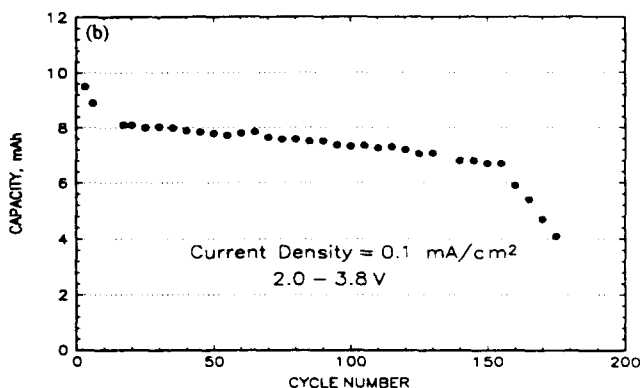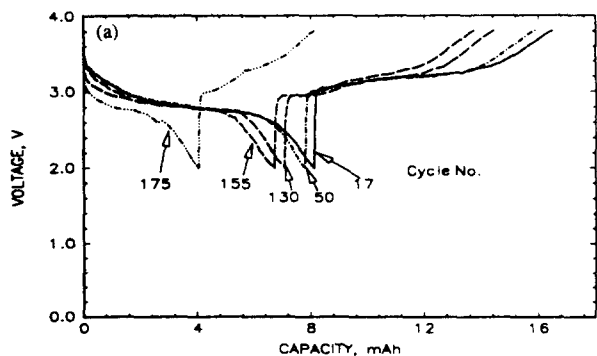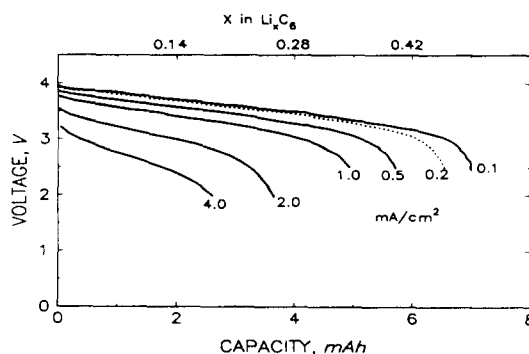

Fig. 10. Rate–capacity behavior of a carbon/LiNiO$_2$ cell containing a PAN-based polymer electrolyte. The carbon anode had a capacity of 7.7 mAh based on an intercalation stoichiometry of Li$_{0.5}$C$_6$. The capacity for the LiNiO$_2$ cathode was 9.4 mAh based on Li$_{0.5}$NiO$_2$.

appearance. The figure-of-merit for the cycling of the Li electrode was 8.3.

The good charge and discharge characteristics of rechargeable Li cells fabricated with PAN- and PVC-based polymer electrolytes is evident from the data in Figs. 7 to 9. The gradual decay in capacity observed in both cases can mostly be attributed to the passivation and loss of the Li anode by its reaction with the electrolyte exacerbated by the low electrode stack pressure in these cells.
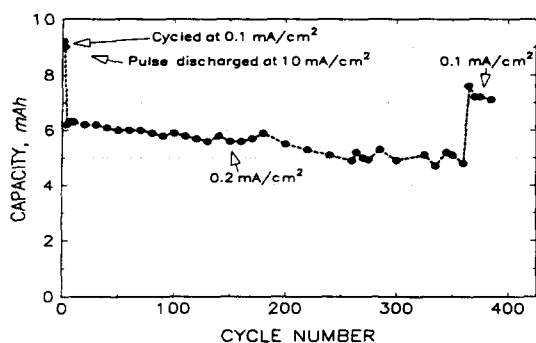
Fig. 11. Discharge capacities as a function of cycle number of a carbon/LiNiO₂ cell containing a PAN-based polymer electrolyte. The carbon electrode had a capacity of 9 mAh.
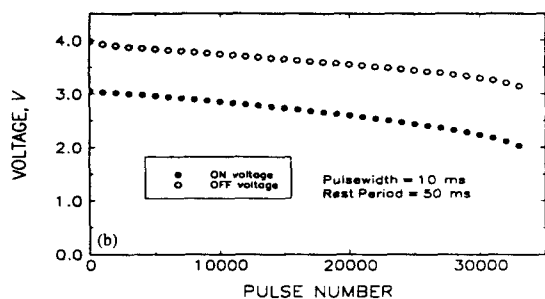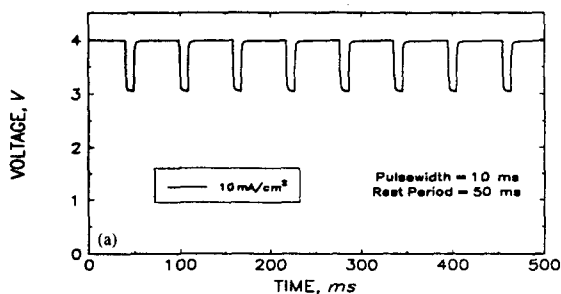

Fig. 12. (a) Typical voltage traces of a carbon/LiNiO₂ cell pulse discharge at a current density of 10 mA/cm² at room temperature, and (b) the ON and OFF voltages during pulsing.
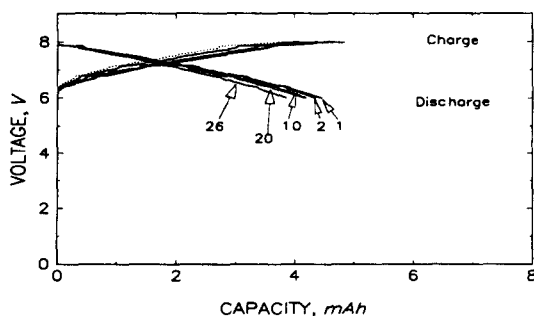

Fig. 13. Charge/discharge cycles of a two-cell carbon/LiNiO₂ bipolar battery. The battery was cycled at 0.25 mA/cm² between 5.0 and 8.0 V.

2.4. Performance of rechargeable Li-ion cells and bipolar batteries

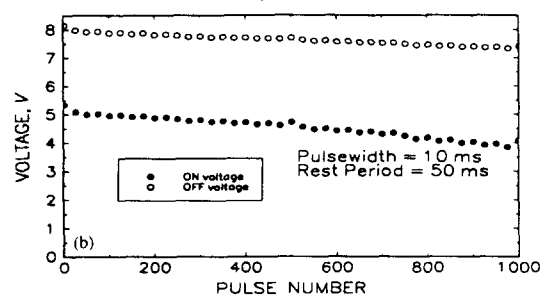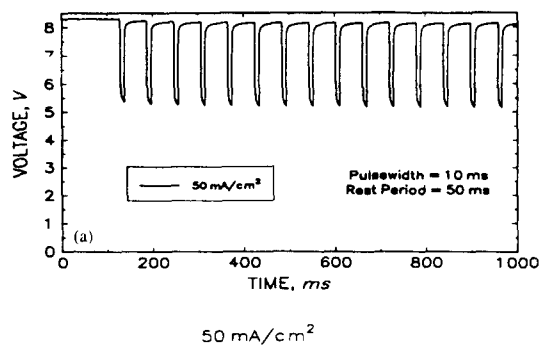Rechargeable Li-ion cells fabricated with the PAN- or the PVC-based electrolytes have demonstrated at-

Fig. 14. (a) Typical pulses of the carbon/LiNiO₂ bipolar battery at 50 mA/cm², and (b) the ON and OFF voltages during pulsing.

tractive charge/discharge behavior. The anodes in these cells consisted of graphitic carbon based on petroleum coke. This carbon electrode reversibly intercalates 0.4 to 0.5 Li/C₆ in cells containing the PAN-based polymer electrolytes. The layered compound LiNiO₂ was used as the high voltage cathode. It delivers a reversible capacity of about 170 mAh/g when cycled between 4.2 and 3.0 V in a Li cell.

Fig. 10 shows the rate–capacity data for a carbon/LiNiO₂ cell, containing a PAN-based polymer electrolyte, discharged at a series of currents from 0.1 to 4.0 mA/cm². The cell capacity was limited by that of the carbon anode. At 0.1 mA/cm², the cell delivered almost 100% of the capacity at a load voltage of 3.7 V. At the highest current density of 4.0 mA/cm², the cell delivered about 40% of the capacity at a load voltage of 2.5 V.

The excellent cycleability of the carbon/LiNiO₂ cell containing the PAN-based polymer electrolytes is exemplified by the data in Fig.11. The cell was first cycled continuously at 0.1 mA/cm², followed by pulsed discharge at a current density of 10 mA/cm². Thereafter, it was cycled at 0.2 mA/cm² for 375 times. At the end of this cycling, the cell retained 85% of the initial discharge capacity at this rate, suggesting attractive rechargeability for this cell. On lowering the discharge current to 0.1 mA/cm², the capacity increased to 7 mAh. Cycling of this cell is still continuing.

Fig. 12 shows typical pulsed discharge data for the cell at 10 mA/cm² for a pulse width of 10 ms. The data indicate fast response of the cell voltage to the applied current as well as rapid recovery of the open-circuit voltage when the discharge current was turned

off. The initial load voltage was about 3 V and a total of 30 000 pulses to a cutoff of 2.0 V were obtained. The total capacity of these pulses was very close to the theoretical value.

Polymer electrolytes are suitable for the construction of solid-state bipolar batteries, by stacking up laminates of these electrolytes and bipolar electrode plates. Two-cell carbon/$LiNiO_2$ bipolar batteries we have fabricated using PAN-based electrolytes have shown good cycling behavior and high current pulsing capability. Typical data for the continuous cycling of such a battery between 5.0 and 8.0 V at 0.25 mA/cm^2 are given in Fig. 13. The battery could be discharged at pulse currents as high as 50 mA/cm^2 (Fig. 14). These data were acquired using anodes and cathodes of about 75 μm thickness. It is expected that with thinner electrodes and electrolytes the rate capability of these cells and batteries can be further improved.

3. Conclusions

The PAN- and the PVC-based plasticized polymer electrolytes possessing room temperature conductivities of $> 10^{-3} \Omega^{-1}$ cm^{-1} have been found to have adequate stability in contact with the metallic Li anode to fabricate Li batteries. Rechargeable Li/$Li_xMn_2O_y$ and carbon/$LiNiO_2$ cells have demonstrated high rate discharge capability and good rechargeability at room temperature yielding rates as high as the C-rate and several hundred full depth cycles. They are thus promising candidates for use as long cycle-life rechargeable batteries for various applications. Two-cell carbon/$LiNiO_2$ bipolar

batteries could be discharged at pulse currents as high as 50 mA/cm^2.

Acknowledgements

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