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FACTORS INFLUENCING THE DISCHARGE CHARACTERISTICS OF $NA_{0.44}MNO_2$-BASED POSITIVE ELECTRODE MATERIALS FOR RECHARGEABLE LITHIUM BATTERIES

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ABSTRACT

Cathode materials with the $Na_{0.44}MnO_2$ structure are highly reversible towards lithium insertion processes, resist conversion to spinel and are not easily damaged by abuse through over-charging or over-discharging. While the theoretical capacity of Li_xMnO_2 made from $Na_{0.44}MnO_2$ is at least 200 mAh/g, in practice only about 45-60% utilization is obtained in lithium cell configurations, in part because not all of the lithium can be extracted below the oxidative stability limit of the electrolyte. Higher utilization is obtained in cells with partially exchanged materials, which have larger unit cells, but *in-situ* exchange processes lead to an apparent capacity fade upon cycling. The benefits of the larger unit cell without the complications of such exchange processes may be realized by replacing some of the manganese with titanium in the structure. A series of compounds with the formula $Li_xTi_yMn_{1-y}O_2$, where y=0.11, 0.22, 0.33, 0.44, and 0.55 was synthesized and characterized for this study. A maximum reversible capacity of 150 mAh/g between 2.5 and 3.5V vs. Li was obtained for $Li/P(EO)_8LiTFSI/Li_xTi_{0.22}Mn_{0.78}O_2$ cells at 85° C in electrochemical potential spectroscopy experiments. Cells with the titanium-doped manganese oxides exhibited a fade rate of 0.12% or less per cycle, indicating that the increased utilization does not come at the expense of cyclability.

INTRODUCTION

Lithium ion-exchanged materials made from $Na_{0.44}MnO_2$ have recently been used as positive electrodes in rechargeable lithium battery configurations.[1,2,3] These cathodes show a high degree of reversibility towards intercalation processes and are unusually resistant to degradation when over-charged or over-discharged.[4] Furthermore, conversion to the thermodynamically favored spinel structure does not occur below about 400° C, nor does degradation occur upon cycling at elevated temperatures. $Na_{0.44}MnO_2$ has an unusual double tunnel structure which can accommodate intercalation and de-intercalation of either Na or Li ions without undue stresses, rendering it extremely robust. This makes it attractive for use in electric vehicle batteries, in which abuse situations such as over-charging and -discharging are likely to occur.

$Na_{0.44}MnO_2$ is readily made by reacting together solid state precursors at elevated temperatures. The material may be used as-is, or ion-exchanged prior to use in a lithium battery configuration,. Partial substitution of Li for Na occurs under mild conditions, but full exchange occurs in molten $LiNO_3$ or $LiNO_3/KNO_3$ solutions above 200° C. The resultant products are isostructural to the parent compound.[2]

For this compound, all sites in the tunnels are full at a composition of $Na_{0.66}MnO_2$, corresponding to ~200 mAh/g theoretical capacity for reversible sodium intercalation. Higher capacities may be possible in lithium batteries because of the smaller size of the Li^+ ion, and because these ions are probably located in sites different than those for sodium. In operating Li cells with liquid or polymer electrolytes, the shape of the discharge profile varies with extent-of-exchange and conditions, and determines utilization between set voltage limits. Voltage limits are selected for compatibility with solvents and electrolytes and to minimize power loss during operation. For highly exchanged samples, discharge profiles are more steeply sloping, and less capacity is accessed, because it is not possible to fully extract Li upon charge (cells are assembled in the partially discharged state, and initially charged). This is most likely due to the smaller unit cells of exchanged samples (680 $Å^3$ for $Na_{0.44}MnO_2$ compared to 608 $Å^3$ for $Li_{0.27}MnO_2$).[2]

Electrochemical potential spectroscopy experiments on Li/Li_xMnO_2 cells[2] show that lithium insertion processes are highly reversible. No capacity fading[3] is seen during galvanostatic cycling when the lower cell voltage limit is set above 2.5V. Although materials that still contain Na^+ ions exhibit more discharge capacity initially, the cycling performance is poorer. This is due to a slow *in situ* exchange, which increases the slope of the voltage profile. The best compromise between cycling performance and initial capacity is found with partially exchanged materials. Sodium ions prop open the tunnels (e.g., the unit cell volume of $Na_{0.23}Li_{0.21}MnO_2$ is 661 $Å^3$) allowing de-intercalation of the mobile Li ions. If cells are not charged to high voltages, Na does not diffuse out, and the discharge characteristics do not change, preventing the apparent capacity loss.

It is preferable to build a larger unit cell by substitution of Mn in the metal oxide framework rather than by pillaring tunnels with sodium ions, because of the possibility of

overcharge in the intended applications. This can be done by substituting Mn in the framework with a larger ion such as Ti. Herein, we report preliminary results obtained on a series of compounds, $Li_xTi_yMn_{1-y}O_2$, with y=0.11, 0.22, 0.33, 0.44, and 0.55.

EXPERIMENTAL

$Na_{0.44}Ti_yMn_{1-y}O_2$ with y=0, 0.11, 0.22, 0.33, 0.44 and 0.55 was made by heating together well-mixed powders of $Na_2Ti_3O_7$, Mn_2O_3 and Na_2CO_3 in the desired proportions at 850° C for ten hours. Best results were obtained when a slight excess of Na (0.47-0.5 Na/M, where M=Mn+Ti) was used, due to some loss of sodium during heating. In cases where Mn_2O_3 impurities were still detected, powders were re-ground with NaOH and re-fired. The products obtained after this treatment were phase-pure according to the x-ray powder diffraction patterns, and were black or brown-black in color.

$Na_{0.44}Ti_yMn_{1-y}O_2$ powders were ion-exchanged by heating them in a molten salt mixture of 68 mol% $LiNO_3$/32 mol% KNO_3 above the melting point (200° C). Enough of the salt mixture was used so that there was a two-fold excess of Li, and the mixture was poured out and replaced twice during the exchange, which typically took 48 hours. ICP analysis carried out at the Earth Sciences Division analytical laboratory at Lawrence Berkeley National Laboratory indicated a mole ratio of 0.47Li:0.027Na:0.0037K:Mn for the sample with no titanium. Samples containing titanium were insoluble and thus could not be chemically analyzed, but x-ray powder diffraction patterns indicated single phases with unit cells considerably smaller than the sodium-containing starting materials.

Electrodes for liquid electrolyte cells were fabricated by mixing together the electroactive material, acetylene black (Chevron Chemical Company, Cedar Bayou Plant, Baytown TX) and ethylene/propylene/diene terpolymer (EPDM, Aldrich Chemical Company) in cyclohexane in a 79:20:1 ratio. The mixture was then cast onto stainless steel disks or Lydall Technimat 6100-035 carbon paper and dried. Loading was typically 5-15 mg/cm^2. Cells were then assembled by stacking the porous electrodes, Celgard 3401, lithium metal discs (Cyprus-Foote Mineral Co., Kings Mountain, NC), metal backing plates, and wave washers in 2032 coin cells and pressing together, after wetting with electrolyte solution (1M $LiPF_6$ in 1:2 EC/DMC, EM Industries, Darmstadt, Germany).

Composite polymer electrodes and polymer cells were fabricated as described previously.[1] Cells were equilibrated at 85±0.5° C in a convection oven equipped with a Eurotherm controller for at least one hour prior to testing.

A Siemens D5000 diffractometer was used to obtain x-ray powder diffraction patterns, and Powder Cell 2.0 for Windows (W. Kraus and G. Nolze, Federal Institute for Materials Research and Testing, Rudower Chaussee 5, 12489 Berlin, Germany) was used to refine the data and obtain unit cell parameters. A MacPile II from Bio-Logic, SA, Claix France was used for both galvanostatic and potentiostatic experiments. For electrochemical potential spectroscopy experiments, the potential was stepped 10 mV/4 hours, or until the current had decreased to 1/1000 of its initial value, between 2.5 and 3.5V.

RESULTS AND DISCUSSION

Electrochemical potential spectroscopy experiments on lithium polymer cells at 85°C and liquid electrolyte cells at room temperature show that Li_xMnO_2 has excellent reversibility towards lithium insertion processes in both configurations. Cells typically deliver about 80-90 mAh/g between 2.5 and 3.5V, and an additional 20-40 mAh/g between 3.5 and 4.0V under these near-equilibrium conditions. An analysis of the $i^{1/2}$ vs t behavior for each 10 mV step in potential[5] shows that lithium diffusion coefficients decrease by nearly two orders of magnitude near 2.5V, and by about 4 orders of magnitude above 3.4V. This suggests that low utilization during galvanostatic discharge between set voltage limits may be caused, in part, by slow diffusion near the end of charge and discharge. The observed correlation[2] between unit cell size and utilization between set voltage limits may therefore be, in part, due to a kinetic effect.

Figure 1 shows galvanostatic discharges of two Li/1M $LiPF_6$, 1:2 EC-DMC/Li_xMnO_2 cells at 0.53 mA/cm^2 (approximately C/2). Cell E4 contains the as-made Li_xMnO_2, while Cell A8 contains a sample that was attritor-milled prior to use. The expected capacity was delivered by cell A8, while cell E4 delivered considerably less. The difference is attributable to the smaller particle size of the attritor-milled sample, which decreases the lithium diffusion path-length and the over-potential near the end of discharge. Figure 2 shows discharges at several different rates for cell A8. Utilization falls off only slightly when the rate is doubled, suggesting that kinetic limitations are no longer controlling the behavior of the manganese oxide electrode. Figure 3 shows that there is essentially no capacity loss for this electrode after forty cycles. Thus, higher utilization does not come at the expense of reversibility for this material. However, higher capacities within a fairly narrow voltage range are still needed for practical applications, including electric vehicles.

Increased capacity can only be achieved by modifying the discharge profile to make it less steep, e.g., by admetal doping. This is particularly critical if this material is to be used in a polymer electrolyte cell configuration, because common PEO-based polymer electrolytes are oxidized above 4.0V vs. Li (the exact stability limit varies with the salt used and the operating temperature). Substitution with ions that are larger than Mn^{4+} (e.g., Ti^{4+}) are expected to result in larger unit cells and better utilization below this voltage. The existence of an isostructural compound, $Na_4Ti_5Mn_4O_{18}$[6] (i.e., "$Na_{0.44}Ti_{0.55}Mn_{0.45}O_2$") indicates that up to 55 atom% Ti can be substituted for Mn. A series of materials, $Na_{0.44}Ti_yMn_{1-y}O_2$, with y=0.11, 0.22, 0.33, 0.44 and 0.55 were synthesized and ion-exchanged for this study. The unit cell size increases monotonically as more Mn is replaced with Ti.

Figure 4 shows pseudo-open circuit voltage profiles derived from electrochemical potential spectroscopy experiments for several Li/$P(EO)_8$LiTFSI/$Li_xTi_yMn_{1-y}O_2$ cells at 85° C. While most of the capacity is still delivered between about 3.4-2.8V vs Li, it is clear that the discharge characteristics have been modified by the admetal doping. Voltage profiles are flatter and more capacity is available between 2.5 and 3.5V. The best results are obtained for $Li_xTi_{0.22}Mn_{0.78}O_2$ which delivers up to 150 mAh/g under these conditions; nearly twice as much as Li_xMnO_2. It is noteworthy that while capacity

increases with Ti content up to about 22-33 atom% substitution, it decreases for y=0.44 and 0.55, suggesting that Ti is not electroactive under these conditions. It should be noted that, in theory, up to 33% of Mn could be substituted with a redox-inactive metal without having a discernible effect on capacity, since insertion is site-limited.

Figure 5 shows galvanostatic discharges at 0.1 mA/cm^2 (approximately C/3) for Li/P(EO)$_8$LiTFSI/$Li_xTi_yMn_{1-y}O_2$ cells at 85° C. While the Ti-doped samples, with the exception of y=0.55, discharge farther than undoped Li_xMnO_2, they deliver less capacity than the ECPS experiments predict. This suggests that there is a kinetic limitation preventing full utilization. It should, however, be possible to engineer the particle size and surface area to improve the rate capability as with Li_xMnO_2. Figure 6 shows cycling data for several Li/P(EO)$_8$LiTFSI/$Li_xTi_yMn_{1-y}O_2$ cells at 85° C. The excellent reversibility that is characteristic of the $Na_{0.44}MnO_2$ structure is retained for the Ti-doped materials with higher capacity. Even at this elevated temperature, a capacity loss of only 0.12%/cycle was observed for the Li/P(EO)$_8$LiTFSI/$Li_xTi_{0.22}Mn_{0.78}O_2$ cell, and only 0.07%/cycle for the Li P(EO)$_8$LiTFSI/$Li_xTi_{0.44}Mn_{0.56}O_2$ cell.

CONCLUSIONS

Li_xMnO_2 made from $Na_{0.44}MnO_2$ is an extremely robust and reversible cathode material with voltage characteristics that are compatible with polymer electrolytes. Rate capability and utilization can be improved by decreasing particle size without compromising cycling; forty cycles in a liquid electrolyte cell configuration at room temperature were obtained at 0.53 mA/cm^2 with complete capacity retention. While the performance is impressive, better utilization is still needed for practical applications. Materials with the $Na_{0.44}MnO_2$ structure, in which some of the Mn is replaced with Ti ($Li_xTi_yMn_{1-y}O_2$), exhibit increased capacity between 2.5 and 3.5V in a polymer cell configuration, and still cycle well. While as much as 150 mAh/g can be obtained for $Li_xTi_{0.22}Mn_{0.78}O_2$ cathodes according to electrochemical potential spectroscopy experiments, in practice less is realized during galvanostatic discharges. This suggests a kinetic limitation similar to that seen in the parent compound. It may be possible to overcome this by decreasing the particle size, as with Li_xMnO_2 made from $Na_{0.44}MnO_2$.

ACKNOWLEDGMENTS

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FIGURES

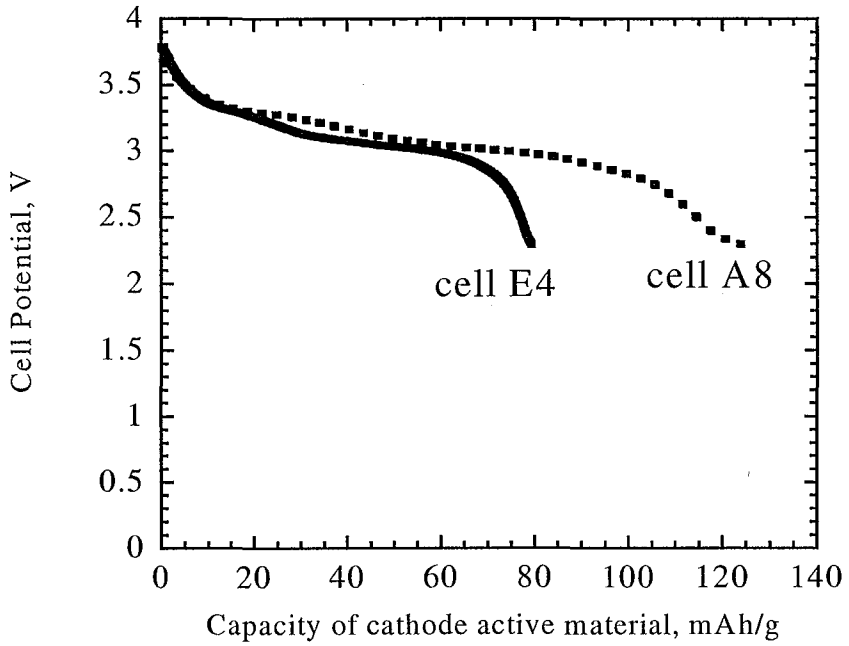

Figure 1. Galvanostatic discharges at 0.53 mA/cm^2 for Li/1M $LiPF_6$, EC-DMC/Li_xMnO_2 cells at room temperature. Cell E4 (—) was fabricated using as-made material, while cell A8 (''''') contained attritor-milled material.

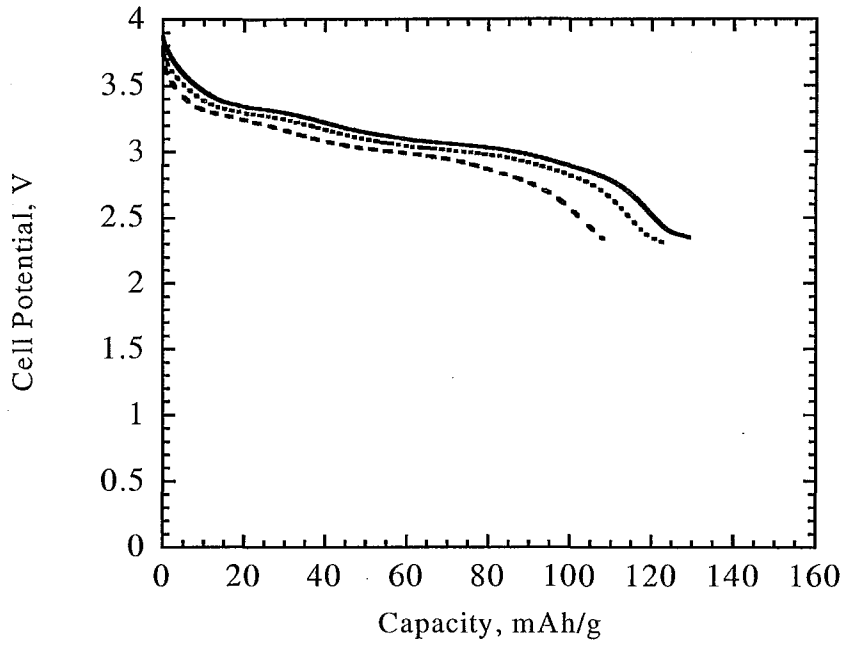

Figure 2. Galvanostatic discharges of a Li/1M $LiPF_6$, EC-DMC/Li_xMnO_2 cell (cell A8) at 0.11 mA/cm^2 (—), 0.53 mA/cm^2 (''''''), and 1.06 mA/cm^2 (----).

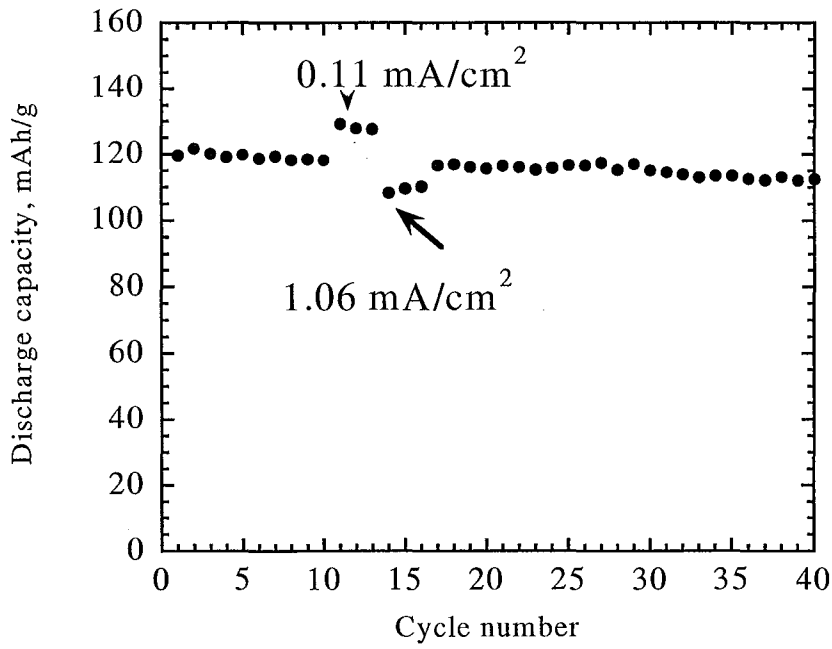

Figure 3. Capacity as a function of cycle number for cell A8 between 4.0 and 2.35V. Unless otherwise noted, all discharges were at 0.53 mA/cm^2.

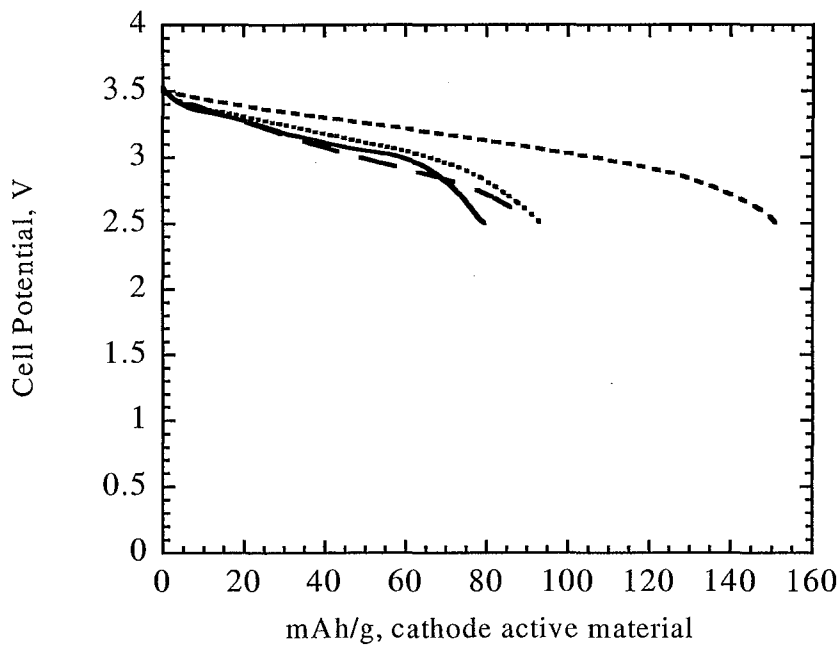

Figure 4. Pseudo-open circuit potential profiles obtained from electrochemical potential spectroscopy experiments on Li/P(EO)$_8$LiTFSI/Li$_x$Ti$_y$Mn$_{1-y}$O$_2$ cells at 85° C; y=0 (—), y=0.11 (''''), y=0.22 (-----), and y=0.44 (- - -). Cells were stepped 10 mV/4 hours between 3.5 and 2.5V and back again.

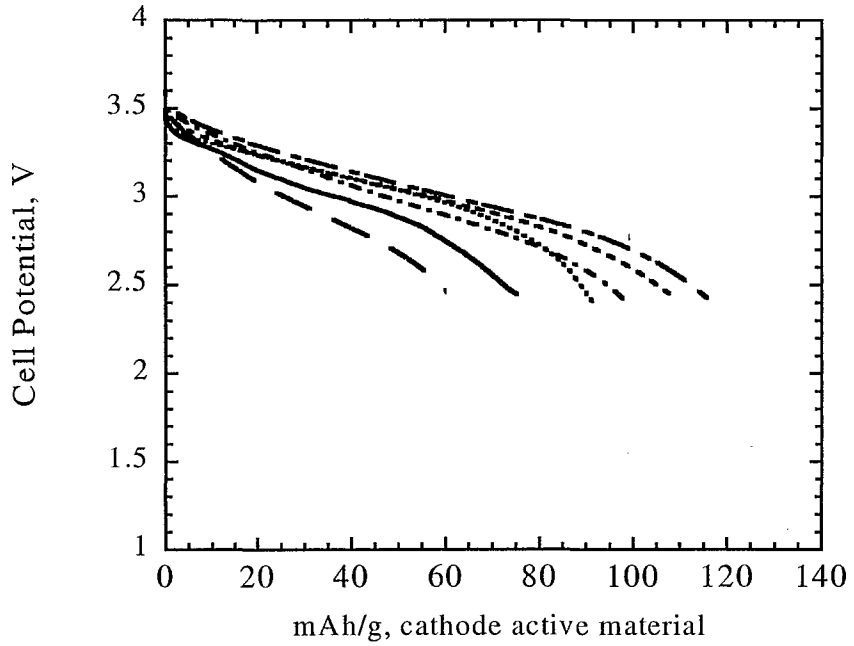

Figure 5 (left). Galvanostatic discharges for Li/P(EO)$_8$LiTFSI/Li$_x$Ti$_y$Mn$_{1-y}$O$_2$ cells at 85° C (0.1 mA/cm^2); y=0 (—), y=0.11 (···), y=0.22 (---), y=0.33 (- –) y=0.44 (· –), y=0.55 (– –).

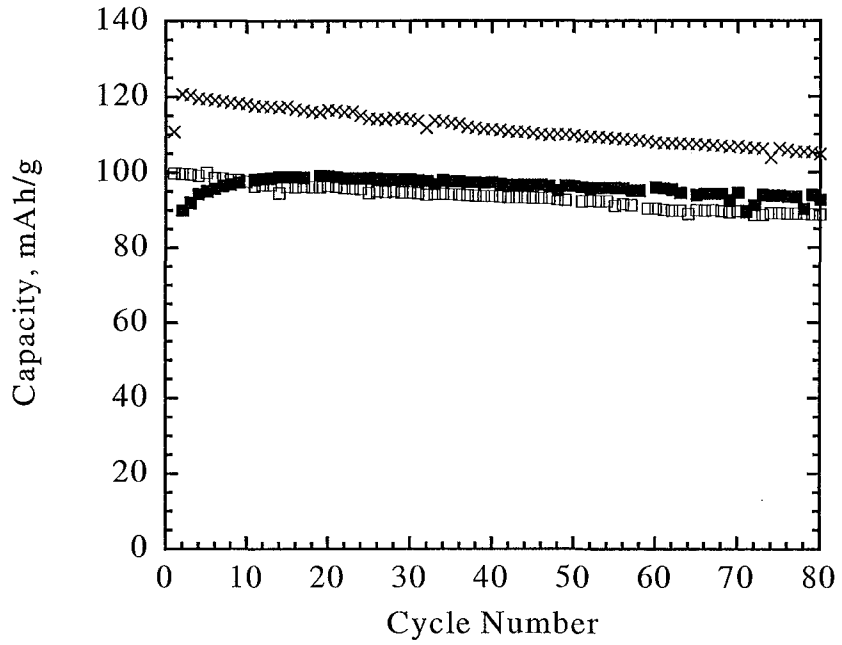

Figure 6. Capacity of Li/P(EO)$_8$LiTFSI/Li$_x$Ti$_y$Mn$_{1-y}$O$_2$ cells as a function of cycle number at 85° C; y=0.11 (□), y=0.22 (x), and y=0.44 (■). Cells were discharged between 3.6 and 2.4V at 0.1 mA/cm^2.