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ABSTRACT

Specific discharge capacities in excess of 200 mAh/g and good reversible cycling behavior between 3.8 and 2.0 V has been observed in a lithium cell for α -MnO₂ phases with the hollandite structure. A combination of lithia (Li₂O) doping and ammonia (NH₃) treatment of the active material powder having the composition α -[0.143 Li₂O]•[0.007 NH₃]•MnO₂ gave the best electrochemical performance in liquid organic electrolyte (1:1 EC:DMC, 1 M LiPF₆) coin cells, with metallic Li as the negative electrode. The added lithia forms a defect close-packed array of oxide anions and stabilizes the interior of the 2x2 tunnel of the hollandite structure by partially filling the crystallographic position (0,0,0.5) of the tetragonal unit cell (I4/m) with O²⁻ from the added Li₂O. Ammonia treatment is hypothesized to partially fill other lattice vacancies still available within the 2x2 tunnel with the nitrogen atoms from NH₃ taking the same position as the oxide anion in the array. The NH₃ can further stabilize the cell during lithium insertion/extraction because of its favorable hydrogen bonding ability and Lewis base characteristics.

INTRODUCTION

Positive electrodes of manganese oxides that operate at 3 V in lithium (Li) cells compare favorably with 4-V Li/Li_xMn₂O₄ (spinel) cells, based on calculations of achievable energy densities [1]. Theoretically, if a stable Li_xMnO₂ electrode can deliver a practical capacity of 180 mAh/g ($x_{\max} = 0.6$) at an average discharge voltage of 2.8 V, then the system attains an overall energy density of 504 Wh/kg, based on the masses of the active electrode materials only. In terms of stored energy therefore, a 3-V system therefore can compete with conventional 4-V Li-ion cells, which deliver approximately 480 Wh/kg when utilizing LiMn₂O₄ spinel having a practical 120 mAh/g capacity.

Various MnO₂ structure types can be stabilized for lithium insertion/extraction by reacting the MnO₂ frameworks with lithia (Li₂O) [2]. Examples of lithia-stabilized compositions and structures include the α -MnO₂ (hollandite) structure (0.15 Li₂O•MnO₂) [3], ramsdellite-MnO₂ (0.15 Li₂O•MnO₂), the 3-V spinel structure Li₄Mn₅O₁₂ (0.40 Li₂O•MnO₂), and a layered structure derived from the rocksalt phase Li₂MnO₃ (Li₂O•MnO₂) [4].

For the last few years, we have focused on synthesizing new stabilized α -MnO₂ and layered materials and on studying their structures [3-7]. The project objective has been to synthesize and produce a stable host cathode material structure that could reversibly deliver 180 mAh/g capacity at an average 3-V vs. Li. In this paper, we report the most up-to-date results of cycling for a number of coin cells that were built from optimized and stabilized α -MnO₂ compositions. Specific discharge capacities in excess of 200 mAh/g and good cycling behavior

have been observed with electrodes fabricated from lithia-stabilized α - MnO_2 , in cases where the structure has been treated with ammonia (NH_3) gas.

EXPERIMENTAL

All α - MnO_x materials reported in this paper were prepared by reaction of Mn_2O_3 with sulfuric acid. Details of this reaction can be found in previous communications [7-8]. Stabilization of the α - MnO_2 was achieved by introducing lithia into the 2x2 tunnel of the structure. The lithia-doping results in α -[x Li_2O]• MnO_2 ($0 < x \leq 0.15$) which has improved electrochemical properties over the non-lithia-doped parent material. Synthesis of the lithia-doped phases has been previously described [3].

Reactions with ammonia gas were carried out under a number of variable conditions. Different starting material α - MnO_2 (heat-treated or hydrated) powders or α -[x Li_2O]• MnO_2 ($0 < x \leq 0.15$) powders were used. Different reaction times and temperatures were used for these experiments. Powders were loosely placed in alumina trays for firing in a tube furnace. The atmosphere was 4% NH_3 gas flowing in a balance of argon gas. Samples were kept at temperature overnight (10-16 h). Note that this synthesis method differs from that used in previous studies to produce ammonium manganese dioxide (NH_4) Mn_8O_{16} hollandite [9-10]. The quantity of available nitrogen in the samples was determined by combustion at 1000°C, using a LECO CHN-900 analyzer. For this instrument, the accuracy and precision for N is $\pm 2.0\%$, and the detection limit is 0.05 wt.%N. Routine phase analysis was conducted on a Siemens D-5000 X-ray powder diffractometer equipped with Cu K_α radiation.

Li coin cells (size 1225) were constructed with cathode laminates cast from a PVDF (Kynar; Elf Atochem) slurry mix onto Al foil current collectors with a doctor blade in an NMP (N-methylpyrrolidone, Aldrich 99+%) solvent. The final laminates consisted of 8% Kynar, 10% carbon, and 82% active oxide. After oven drying at 70°C in air, final punched laminates were dried at 80°C *in vacuo* prior to cell rolling and assembly in either a dry room with <200 ppm H₂O or a helium glovebox with <5 ppm O₂ and H₂O.

RESULTS AND DISCUSSION

The redox stability of many manganese systems is related to how well the structure can resist the Jahn-Teller crystallographic distortion caused by a high concentration of Mn³⁺(d⁴) ions within the structure at the end of discharge. The number of Mn³⁺ ions produced increases when cells operate at voltages below 3 V, and this imposes a serious impediment to long-term cycle life.

In the search for MnO_x materials, α-MnO₂ has been found to maintain a tetragonal structure upon lithiation [7]. A small, 6.5% volume increase was observed in its approximately half-reduced state (discharged condition) from Li₀MnO₂ to Li_{0.48}MnO₂ [7]. The retention of tetragonal symmetry ensures that the Jahn-Teller effect is accommodated in two dimensions, as opposed to one dimension in the case of Li_{1+x}Mn₂O₄ (0<x<1) spinel electrodes [11]. Lattice imaging and convergent beam electron diffraction have confirmed that structural changes take place in lithiated α-MnO₂ products; the structural changes are believed to be associated with manganese and oxygen diffusion from the α-MnO₂ framework into the (2x2) tunnels and a possible ordering of the electro-inserted Li ions [7]. This results in a modified structure that has greater

tolerance to electrochemical cycling than the parent α - MnO_2 material, but significantly lower capacities (about 100 mAh/g). A preliminary hypothesis based on TEM evidence argues that the α - MnO_2 structure is slowly converted to a defect rock salt phase of Li_xMnO_2 ($x < 1$) with continued cycling [7].

One strategy to counteract the under-utilization of the parent anhydrous α - MnO_2 electrode is to provide some pre-cycling stabilizing component in the structure. We have previously reported an improvement in the rechargeability of this system upon chemical doping with a small to moderate amount of lithia. This addition results in a material, for example α -[0.15 Li_2O]• MnO_2 , that shows better utilization at about 130-150 mAh/g under the same voltage limits [3]. A structural basis for the cause of stabilization was hypothesized. The increased amount of O^{2-} anions in the material acts to block the movement of manganese that would normally follow a structural collapse of the (2x2) tunnels. From neutron diffraction data and Rietveld profile refinement of the tetragonal unit-cell structure, we find that the additional oxygen from Li_2O sits in the special lattice position (0,0,0.5) within the 2x2 tunnels. This additional O^{2-} thus provides increased stability to the 2x2 tunnels, which helps the α - MnO_2 framework to maintain stability towards lithium insertion and extraction. Because the lithium ions in α -[0.15 Li_2O]• MnO_2 only partially occupy their sites, the structure can accommodate additional lithium ions during cycling [3].

Table 1 summarizes our most recent selected button-cell cycling testing on 3-V MnO_2 based systems. The capacities are listed for cathodes made from various formulations of manganese dioxide powders based on the phase α - MnO_2 . The best material (cell #5) in terms of

cyclability was a lithia-stabilized phase, α -[0.15 Li₂O]•MnO₂, that gave 182 mAh/g discharge capacity on the 50th cycle. Therefore, this electrode has met our target objective of 180 mAh/g.

The presence of stabilizing atoms or molecules within the (2x2) tunnel of the α -MnO₂ structure is necessary to suppress the capacity fade of the cell during cycling. Thus, one objective was the continued search for other molecules that may provide such stabilization without compromising electrochemical performance.

The hydrated version of α -MnO₂•nH₂O (n = 0.2-0.36) has its advantages as a starting material for improved 3-V MnO₂ electrodes. The water molecule provides structural stability to the framework and hence gives the powder a long shelf life when stored in air. In addition, prior to its incorporation in a lithium cell, the material may be easily heat-treated in air below 300°C to form an anhydrous version that can subsequently be used in lithium batteries. Finally, for synthesis utility, the water molecule is readily exchangeable with Li₂O and/or mixed Na₂O doping, as well as NH₃ substitution.

NH₃ Stabilization Effects.

A study of the reactions of α -MnO₂ with NH₃ was carried out, with the objective of stabilizing the (2x2) tunnel of α -MnO₂ with NH₃. Ammonia is expected to have a chemistry similar to that of H₂O, particularly with respect to its hydrogen bonding characteristics and molecular neutrality. Molecules of water are known to be accommodated within the (2x2) tunnel of α -MnO₂ [12], so (by chemical similarity) ammonia's reactivity towards α -MnO₂ may be analogous. An additional major advantage of ammonia (substituted for water) is its co-solubility

with metallic lithium. Water, if leached out or lost from the positive electrode, may migrate to react with and destroy the active metallic lithium (negative electrode); in contrast, ammonia, if unexpectedly lost, should cause no degradation of the lithium electrode. As a neutral molecule with base properties, ammonia may also be expected to act to neutralize HF acid impurities within the organic liquid electrolyte, forming NH_4F , a soluble but non-interfering salt, in the Li cell.

The addition of the nitrogen atom of the ammonia group also partially occupies the special position of (0,0,0.5) in the tetragonal unit cell structure (the center of the (2x2) tunnel) [12]. This circumstance is directly analogous to the behavior of the O^{2-} portion of the water molecule in hydrated $\alpha\text{-MnO}_2 \cdot n\text{H}_2\text{O}$ ($0.1 < n < 0.33$), as seen in neutron diffraction experiments [13].

Single-phase X-ray patterns and weight uptake were seen for powders reacted at 125°C in a flow of 4% NH_3 (argon gas balance) for 10 h. Samples heated longer or at higher temperatures form reduced Mn-O impurity phases such as hausmannite Mn_3O_4 . The tetragonal unit-cell a and b parameters of 125°C NH_3 -reacted $\alpha\text{-MnO}_2$ product increases with respect to the heat-treated starting material. Table 2 summarizes the cell parameter results calculated from the lattice parameter least-squares fit of X-ray powder diffraction data.

The increase in the unit-cell volume is only 1.5% for the ammonia-doped sample compared with the hydrated sample. The lack of decrease in unit-cell volume suggests that the ammonia may be substituting for water in the structure. More experimentation will be required to confirm this hypothesis. Table 2 also lists other tetragonal alpha-phase MnO_2 materials that contain either ammonia or ammonium (NH_4^+) cations. Note that the unit-cell is much larger for

a sample containing an NH_4^+ cation inserted in the (2x2) tunnel; this suggests that the prepared sample is more typical of an ammonia-type material.

The incorporation of ammonia in the cathode material ultimately results in cells with significantly improved performance. A series of discharge curves for ammonia-treated $\alpha\text{-MnO}_2$ are shown in Figure 1. The discharge of the electrode is characteristic of an insertion compound. The first discharge shows an extended plateau at about 2.5 V and yields 227 mAh/g when taken down to a cut-off voltage of 2.0 V. With continuous cycling, the curve loses its plateau-type shape and becomes more steeply sloped. The discharge capacity falls off to a steady 167 mAh/g. The stabilized capacity at the 0.2 mA/cm² current rate is the same at discharge number 5 and discharge number 20. This capacity is about 1.7 times that of the unstabilized parent $\alpha\text{-MnO}_2$ electrode.

The cycling stability of the $\alpha\text{-}[0.20 \text{NH}_3]\cdot\text{MnO}_2$ electrode (cell #4) under variable rates is excellent. The inset in Figure 1 charts the discharge capacity delivered by the electrode over 45 cycles. Note that a doubling of the current rate at cycle 26 to 0.4 mA/cm², causes a drop in the capacity of only about 10%. Moreover, the electrode provides a stable capacity at this higher rate.

The utilization and rate characteristics for lithia-doped $\alpha\text{-MnO}_2$ materials can be further improved if the compound is treated with ammonia gas at temperatures below 150°C. Figure 2 shows the voltage profile of a lithia-doped MnO_2 material with composition $\alpha\text{-}[0.143 \text{Li}_2\text{O}]\cdot\text{MnO}_2$. A very large initial discharge capacity of 240 mAh/g is observed for this material, but, after extended cycling, it decreases to 199 mAh/g after 10 cycles. Note that the shape of the first

discharge curve shows two plateaus marked with arrows and labeled as "1" and "2" on the figure. With continued cycling these plateaus merge into one sloping insertion process. This behavior is somewhat different from that of the non-lithia doped α - MnO_2 sample, which exhibits only one extended plateau on the first discharge (Figure 1). When the same sample is tested after ammonia treatment, formulated now as α - $[\text{0.143 Li}_2\text{O}\cdot\text{0.007 NH}_3]\cdot\text{MnO}_2$ (i.e., cell #8 in Table 2 and the inset to Figure 2), it has an initially lower initial discharge capacity of 220 mAh/g. Overall, though, it behaves better than the parent material; in particular there is less fading during the extended cycle life tests. The specific discharge capacity totals from cycle life tests, including a higher C/3 rate (0.4 mA/cm^2) used in these tests, are shown in the inset in Figure 2. The material cycling was excellent; it delivered approximately 150 mAh/g capacity at the higher C/3 rate with good stability. Returning to the lower rate did not affect the utilization; the material came back at 211 mAh/g at the C/12 standard rate (0.1 mA/cm^2).

Figure 3 shows that the cell impedance of the α - $[\text{0.143 Li}_2\text{O}\cdot\text{0.007 NH}_3]\cdot\text{MnO}_2$ electrode material (cell #8, Table 2) decreases after the first break-in cycle, afterward remaining the same with extended cycling. These experiments were carried out by using a 30-sec current-interruption method. The result suggests that the active material is stable over time. Electrodes made of this active material do not increase in polarization with cycling, and lithium-ion diffusion remains constant over many lithium insertion and extraction cycles.

The ratio of stabilizing atoms (O alone, N alone, or O + N) located at the special crystallographic position of (0, 0, 0.5) in the tetragonal unit cell to Mn in the lattice works best at a composition ratio of approximately 0.15. Because the neutron scattering lengths for oxygen and nitrogen are quite different, we intend to undertake further structural studies of the NH_3 -

treated $x\text{Li}_2\text{O}\cdot\text{MnO}_2$ phases, using neutron diffraction techniques, to elucidate the role that O and N atoms play in the $\alpha\text{-MnO}_2$ structure.

CONCLUSION

When lithia doping and ammonia treatment are both implemented in the $\alpha\text{-MnO}_2$ system, excellent cycling properties result. Rechargeable specific discharge capacities greater than 200 mAh/g can be obtained when a lithia-doped $\alpha\text{-MnO}_2$ electrode, the structure of which has been treated with ammonia, is cycled between 3.8 and 2.0 V in lithium cells. This improvement in performance can be attributed to the stabilization of the hollandite framework by the partial occupancy by both oxygen and nitrogen of sites at the center of the (2x2) tunnels.

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**Table 1. Discharge Capacity Summary for Various
Alpha Manganese Dioxide (α -MnO₂) Materials.***

Cell No.	Compound Type	Capacity (mAh/g), Cycle 1	Capacity (mAh/g), Cycle (x)	Capacity (mAh/g), Cycle (y)
1	α -MnO ₂ , dehydrated (pellet)	218	136 (10)	NA
2	α -MnO ₂ , dehydrated (laminar-1)	212	160 (10)	161 (20)
3	α -MnO ₂ , dehydrated (laminar-2)	241	167 (5)	172 (10)
4	α -[0.20 NH ₃]•MnO ₂ (NH ₃ treated)	227	173 (10)	167 (20)
5	α -[0.15 Li ₂ O]•MnO ₂	222	204 (20)	182 (50)
6	α -[0.154 Li ₂ O]•MnO ₂	201	153 (10, 2.3-V cutoff)	136 (20, 2.3-V cutoff)
7	α -[0.143 Li ₂ O]•MnO ₂	240	199 (10)	188 (20)
8	α -[0.143 Li ₂ O•0.007 NH ₃]•MnO ₂ (NH ₃ treated)	219	227 (18)	211 (33)
9	α -[0.11 Li ₂ O•0.04 Na ₂ O]•MnO ₂	188	182 (10)	NA

*Note: These coin-cell 1225 cells configured as Li/DMC:EC, 1M LiPF₆/MnO_x were fabricated with cathode laminates. Unless otherwise specified, the voltage window of cycling is 3.8 to 2.0 V, and the current rate is 0.1 mA/cm².

**Table 2. Unit-Cell Parameters from XRD for NH₃-Reacted Products of α-MnO₂
(Space Group: I4/m)**

Sample No.	Description	Composition	a=b (Å)	c (Å)	Vol (Å ³)
1	Starting material	α-MnO ₂ •0.33 H ₂ O	9.814(3)	2.850(1)	274.5
2	From 1	α-MnO ₂ • 0.20 NH ₃	9.878(4)	2.856(1)	278.7
3	Literature ^[14]	(NH ₃) ₂ Mn ₈ O ₁₆	9.843	2.849	276.0
4	Literature ^[15]	[NH ₄] _{1.4} Mn ₈ O ₁₆	9.899	2.859	280.2

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- Figure 1** Voltage profile for cell #4 (Table 2) from 3.8 to 2.0 V vs. Li using a 1225 coin cell, 0.2 mA/cm² current density, and a laminate electrode of composition α -[0.20 NH₃]•MnO₂. Figure inset is the discharge capacity as a function of cycle number and two different current densities; these data are for the same material (cell #4, Table 2).
- Figure 2** Voltage profile for cell #7 (Table 2) from 3.8 to 2.0 V vs. Li, using a 1225 coin cell, 0.1 mA/cm² current density, and a laminate electrode of composition α -[0.143 Li₂O]•MnO₂ *prior* to ammonia treatment. Figure inset is the discharge capacity as a function of cycle number and variable current density or C-rate for the same material, but *after* treatment with ammonia (cell #8, Table 2).
- Figure 3** Cell area-specific impedance (ASI) measured at 30 sec after current interruption. The active electrode material is α -[0.143 Li₂O•0.007 NH₃]•MnO₂ (NH₃-treated sample). The voltage window was 3.8 to 2.0 V vs. Li, using a 1225 coin cell, 0.1 mA/cm² current density, and a laminate electrode

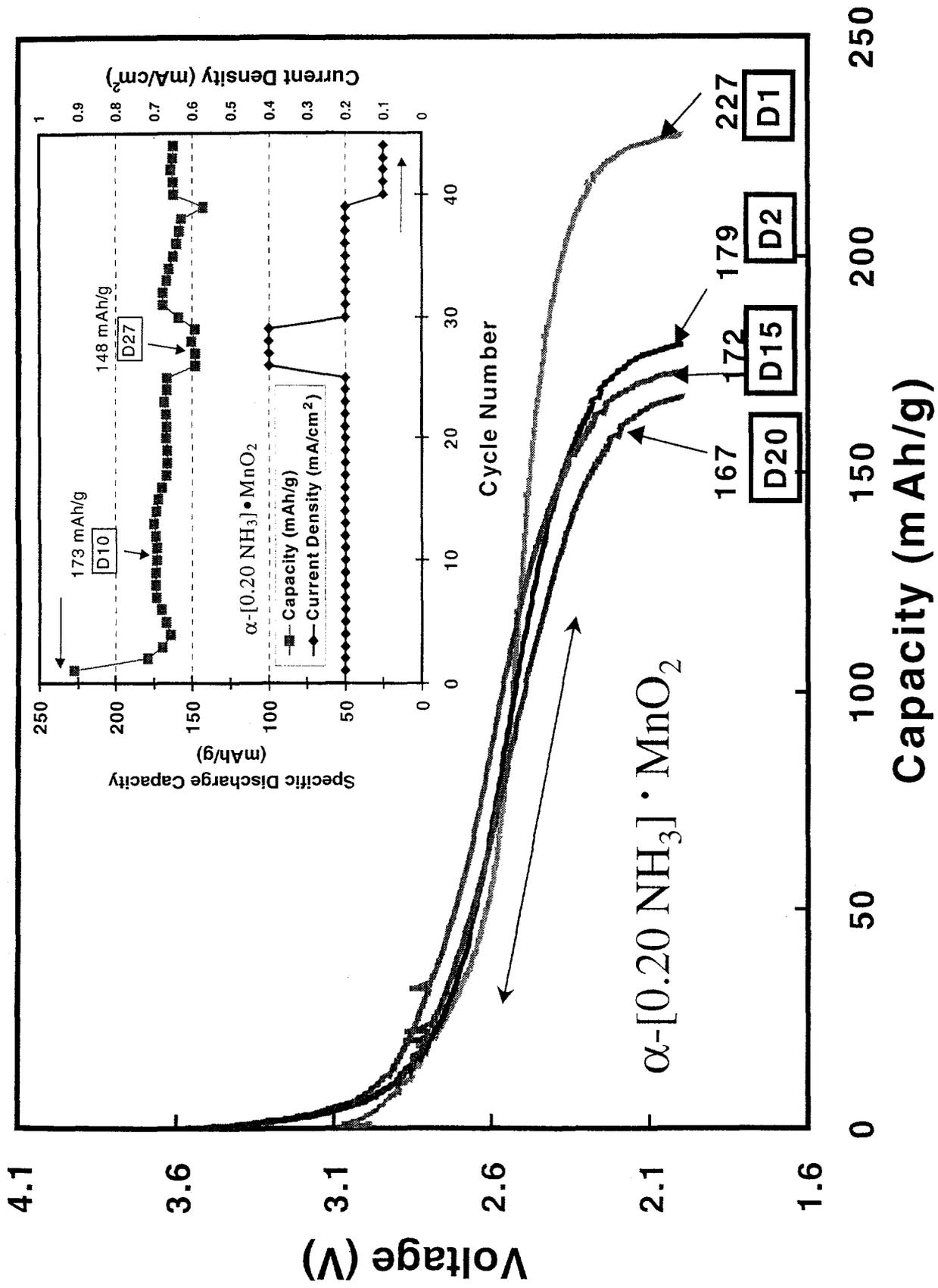


Figure 1

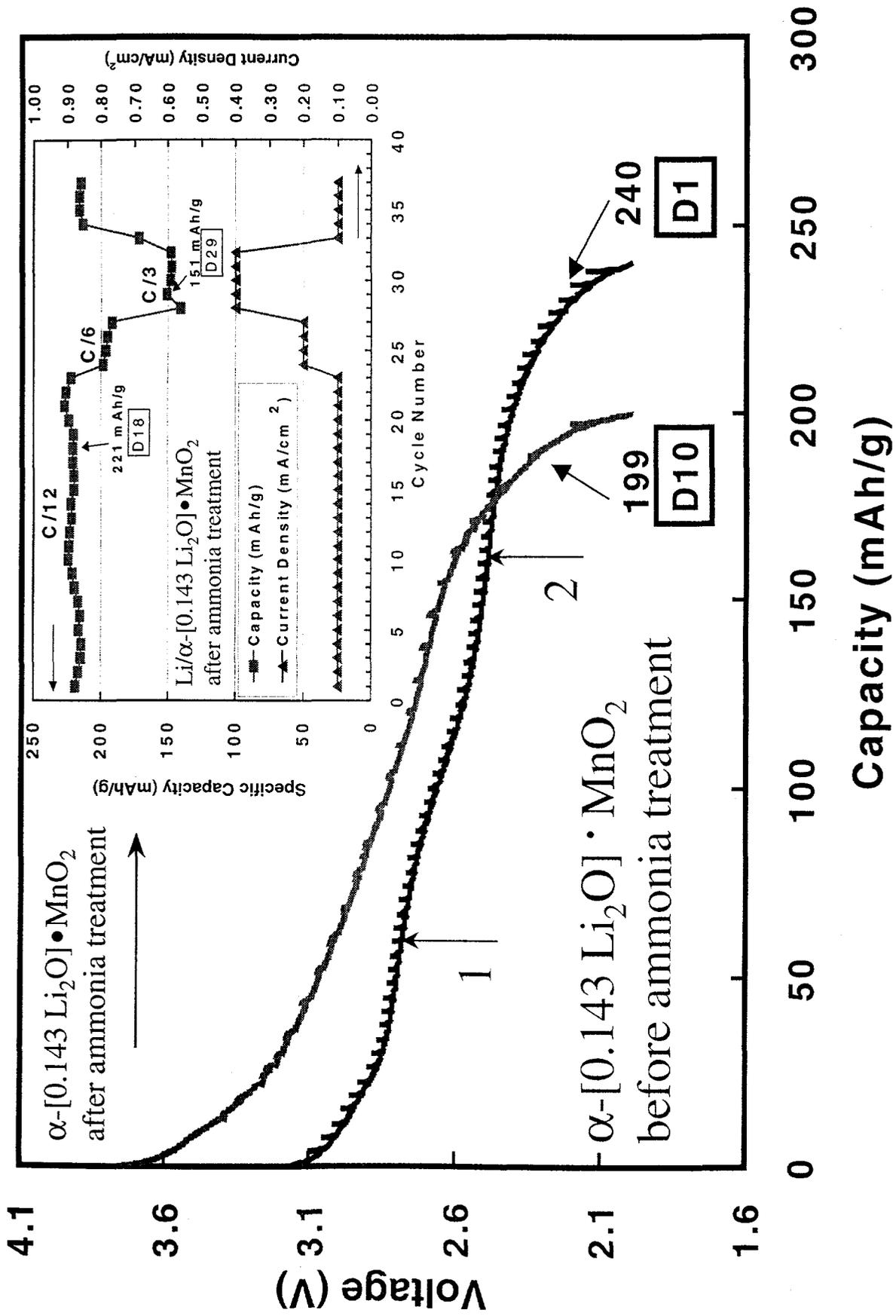


Figure 2

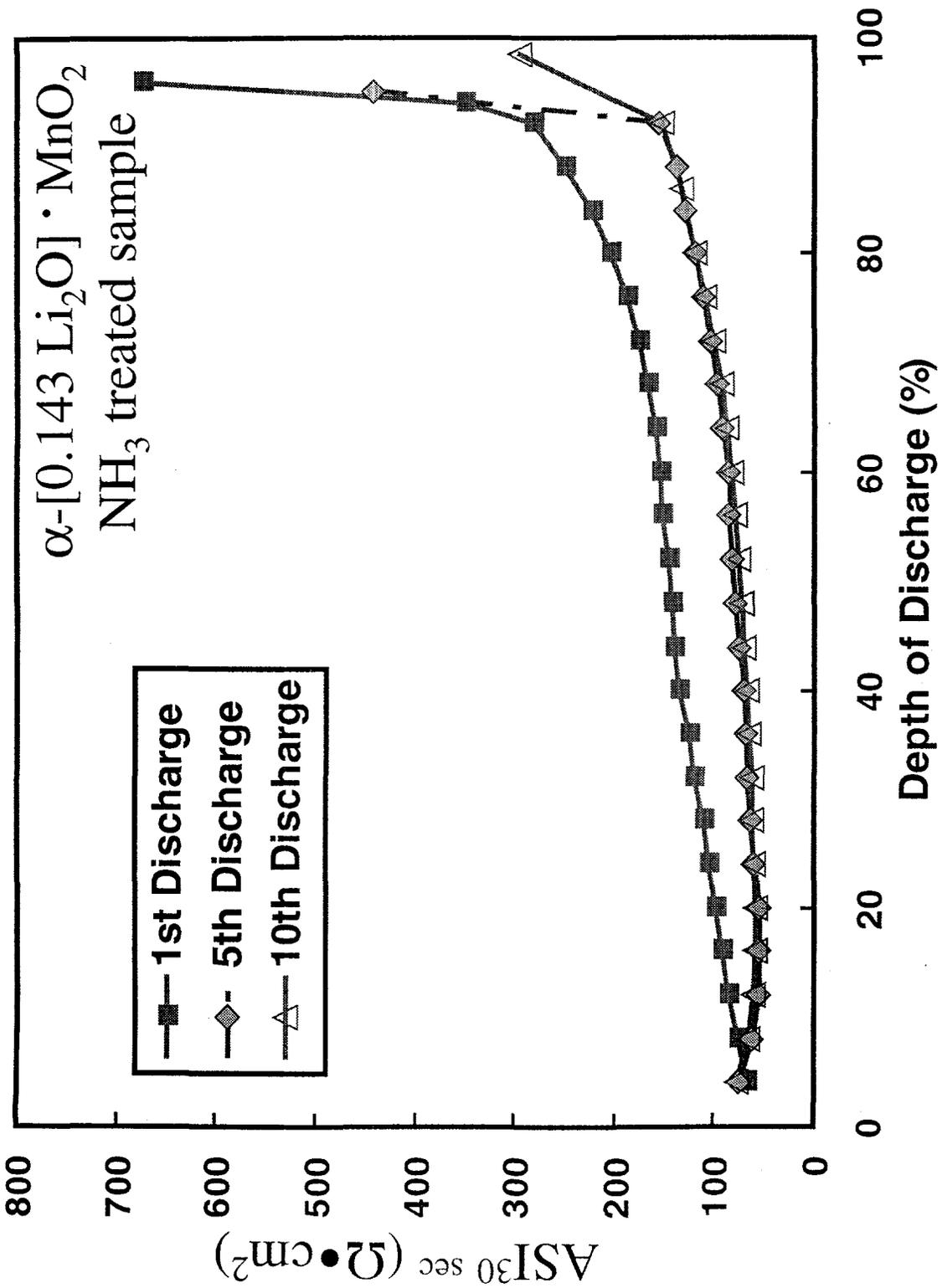


Figure 3