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(54) Title: SODIUM ION BASED AQUEOUS ELECTROLYTE ELECTROCHEMICAL SECONDARY ENERGY STORAGE DEVICE

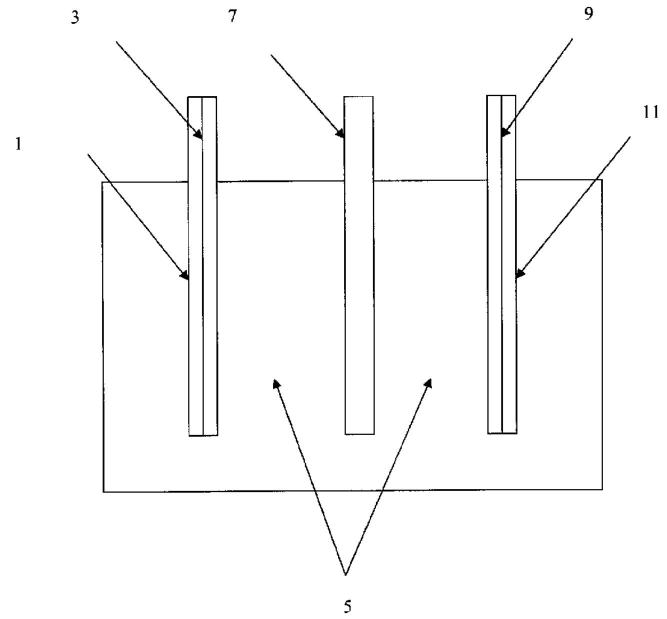
Figure 2

(57) Abstract: A secondary hybrid aqueous energy storage device includes an anode electrode, a cathode electrode which is capable of reversibly intercalating sodium cations, a separator, and a sodium cation containing aqueous electrolyte, wherein an initial active cathode electrode material comprises an alkali metal containing active cathode electrode material which deintercalates alkali metal ions during initial charging of the device.

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SODIUM ION BASED AQUEOUS ELECTROLYTE ELECTROCHEMICAL SECONDARY ENERGY STORAGE DEVICE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority to U.S. Provisional Patent Application Serial Nos. 61/123,230, filed April 7, 2008, 61/129,257, filed June 13, 2008, and 61/154,156, filed 2/20/2009, which are herein incorporated by reference in their entirety.

FIELD OF THE INVENTION

[0002] The present invention is generally directed to aqueous electrolyte electrochemical secondary energy storage devices and materials for use therein.

BACKGROUND OF THE INVENTION

[0003] Small renewable energy harvesting and power generation technologies (such as solar arrays, wind turbines, micro sterling engines, and solid oxide fuel cells) are proliferating, and there is a commensurate strong need for intermediate size secondary (rechargeable) energy storage capability. Batteries for these stationary applications typically store between 1 and 50 kWh of energy (depending on the application) and have historically been based on the lead-acid (Pb-acid) chemistry. Banks of deep-cycle lead-acid cells are assembled at points of distributed power generation and are known to last 1 to 10 years depending on the typical duty cycle. While these cells function well enough to support this application, there are a number of problems associated with their use, including: heavy use of environmentally unclean lead and acids (it is estimated that the Pb-acid technology is responsible for the release of over 100,000 tons of Pb into the environment each year in the US alone), significant degradation of performance if held at intermediate state of charge or routinely cycled to deep levels of discharge, a need for routine servicing to maintain performance, and the implementation of a requisite recycling program. There is a strong desire to replace the Pb-acid chemistry as used by the automotive industry. Unfortunately the economics of alternative battery chemistries has made this a very unappealing option to date.

[0004] Despite all of the recent advances in battery technologies, there are still no low-cost, clean alternates to the Pb-acid chemistry. This is due in large part to the fact that Pb-acid batteries are remarkably inexpensive compared to other chemistries (<$200/kWh), and there is currently a focus on developing higher-energy systems for transportation applications (which are inherently significantly more expensive than Pb-acid batteries).

SUMMARY OF THE INVENTION

[0005] Embodiments of the present invention provide a secondary hybrid aqueous energy storage device comprising an anode electrode, a cathode electrode which is capable of reversibly intercalating sodium cations, a separator, and a sodium cation containing aqueous electrolyte, wherein an initial active cathode electrode material comprises an alkali metal containing active cathode electrode material which deintercalates alkali metal ions during initial charging of the device.

[0006] Other embodiments provide a method of operating a hybrid aqueous energy storage device comprising an anode electrode, a cathode electrode, a separator, and a sodium containing aqueous electrolyte, the method comprising deintercalating alkali ions from an active cathode electrode material during initial charging of the device, reversibly intercalating sodium ions into the active cathode electrode material during discharge cycles, and deintercalating sodium ions from the active cathode electrode during subsequent charge cycles.

[0007] As used herein, the term electronegativity is used to describe the ability of an atom to attract electrons in a covalent bond to itself. Several different scales may be used to describe electronegativity. Unless otherwise indicated, electronegativity values indicated herein are according to the Pauling scale.

[0008] As used herein, the term faradaic reaction indicates a reaction that results in oxidation or reduction of an involved species. For example, in embodiments of the present invention, when Na cations intercalate in to active cathode materials, the active cathode materials must be reduced (that is electrons must be transferred to the active cathode materials) in order to preserve electroneutrality of the bulk material. Conversely, nonfaradaic processes involve the accumulation of charge at the surface of an electrode / solution interface resulting in the formation of an electrical double layer.

[0009] As used herein, the term secondary energy storage device may be used interchangeably with the term secondary battery.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 shows an illustration of one possible charge / discharge mechanism employed by hybrid energy storage devices of the embodiments of the present invention.

[0011] Figure 2 shows a schematic representation of a secondary energy storage device according to an embodiment of the present invention.

[0012] Figure 3 shows the X-ray diffraction pattern obtained from spinel structure $Li_{1.05}Mn_{1.89}Al_{0.06}O_4$ synthesized according the method described in Example 1.

[0013] Figure 4 shows the X-ray diffraction pattern obtained from spinel structure $Mn_{1.89}Al_{0.06}O_4$ (Al-doped λ-MnO_2) after deintercalation of Li from spinel $Li_{1.05}Mn_{1.89}Al_{0.06}O_4$ as described in Example 1.

[0014] Figures 5A and 5B show the overlap of a portion of the X-ray diffraction patterns from Figures 3 and 4.

[0015] Figure 6 shows data from three sequential cyclic voltammargrams for de-lithiated Al-doped λ-MnO_2 active cathode material in aqueous Na_2SO_4 electrolyte obtained after ten conditioning cycles.

[0016] Figure 7 shows cyclic voltammargram data for activated carbon anode material in aqueous Na_2SO_4 electrolyte. No distinct reduction-oxidation peaks are observed.

[0017] Figure 8 shows the charge / discharge behavior (i.e., cell potential versus time through charge / discharge cycles) of a full aqueous Na-ion hybrid energy storage device based on a de-lithiated Al-doped λ-MnO_2 active cathode material in aqueous Na_2SO_4 electrolyte at C/24 and 2C rates.

[0018] Figures 9A and 9B show single C/5 discharge behavior versus time and specific energy (Wh/kg), respectively, for Al-doped λ-MnO_2 active cathode material in aqueous Na_2SO_4 electrolyte from 1.7 to 0.8 V cell potential.

[0019] Figure 10 shows data from a single C/10 discharge cycle as a function of time for Al-doped λ-MnO_2 active cathode material in aqueous Na_2SO_4 electrolyte from 1.7 to 0.6 V cell potential.

[0020] Figures 11A and 11B show data showing the cycling performance of Al-doped λ-MnO_2 active cathode material made via electrochemical Li/Na ion exchange in aqueous Na_2SO_4 electrolyte from 2.0 to 0.8 V cell potential

[0021] Figures 12A and 12B show specific energy and specific capacity, respectively, versus cycle number for long term testing (up to 40 cycles) of a full aqueous Na-ion hybrid energy storage device based on a de-lithiated Al-doped λ-MnO_2 active cathode material in aqueous Na_2SO_4 electrolyte. Figure 12C shows extended high rate cycling performance (cell capacity versus cycle number) for more than 540 cycles at 5C rate across a potential range of 1.8 to 0.8 V.

[0022] Figure 13 shows the energy density as a function of cycle number for Al-doped λ-MnO_2 active cathode material in aqueous 1 M Na_2SO_4 electrolyte with C/5 cycling rate across a potential range of 1.9 to 0.8 V.

[0023] Figure 14 shows specific energy versus discharge rate for a cell with Al-doped λ-MnO_2 active cathode material versus activated carbon anode material in aqueous Na_2SO_4 electrolyte.

[0024] Figure 15 shows specific energy versus specific power for a cell with Al-doped λ-MnO_2 active cathode material versus activated carbon anode material in aqueous Na_2SO_4 electrolyte.

[0025] Figure 16 shows the temperature dependency of specific energy versus discharge rates for cells with Al-doped λ-MnO_2 active cathode material versus activated carbon anode material in aqueous Na_2SO_4 electrolyte.

[0026] Figure 17 shows long term cell capacity performance for a cell with Al-doped λ-MnO_2 active cathode material versus activated carbon anode material in aqueous Na_2SO_4 electrolyte over about 5000 cycles.

[0027] Figure 18 shows the cell potential versus cell energy for a two cell stack constructed with Al-doped λ-MnO_2 active cathode material versus activated carbon anode material in aqueous Na_2SO_4 electrolyte.

[0028] Figure 19 shows the charge / discharge behavior (i.e., cell potential versus time through charge / discharge cycles) of a full aqueous Na-ion hybrid energy storage device based on a $NaMnO_2$ (birnassite phase) active cathode material in aqueous Na_2SO_4 electrolyte.

[0029] Figure 20A shows data from four sequential cyclic voltammograms for $Na_2Mn_3O_7$ active cathode material in aqueous Na_2SO_4 electrolyte solution. Figure 20B shows a potential versus time profile from a portion of the cyclic voltammogram testing shown in Figure 20A.

[0030] Figure 21 shows discharge behavior of a test cell with a Na_2FePO_4F active cathode material, an activated carbon anode material, and aqueous Na_2SO_4 electrolyte.

[0031] Figure 22 shows a structural representation of the crystal structure of $Na_{0.44}MnO_2$ perpendicular to the *ab* plane.

[0032] Figure 23 shows a cyclic voltammogram of a composite $Na_{0.44}MnO_2$ electrode in an aqueous Na_2SO_4 electrolyte.

[0033] Figure 24 shows a cyclic voltammogram of a composite activated carbon electrode in an aqueous Na_2SO_4 electrolyte.

[0034] Figure 25 shows charge / discharge behavior of a composite $Na_{0.44}MnO_2$ / $Na_2SO_{4(aq)}$ / composite activated carbon hybrid electrical energy storage device through five cycles over about 15 hours.

[0035] Figure 26 shows specific capacity across a typical discharge cycle of a composite $Na_{0.44}MnO_2$ / $Na_2SO_{4(aq)}$ / composite activated carbon hybrid electrical energy storage device.

[0036] Figure 27 shows long-term charge / discharge behavior of a composite $Na_{0.44}MnO_2$ / $Na_2SO_{4(aq)}$ / composite activated carbon hybrid electrical energy storage device after 40 continuous hours of testing to about 60 continuous hours of testing.

[0037] Figure 28 shows a plot of charge and discharge capacity as a function of cycle for a composite $Na_{0.44}MnO_2$ / $Na_2SO_{4(aq)}$ / composite activated carbon hybrid electrical energy storage device over 180 cycles.

[0038] Figure 29 shows a plot of charge and discharge energy as a function of cycle for a composite $Na_{0.44}MnO_2$ / $Na_2SO_{4(aq)}$ / composite activated carbon hybrid electrical energy storage device over 110 cycles.

[0039] Figure 30A shows cell potential versus specific capacity for a full aqueous Na-ion hybrid energy storage device based on a composite $Na_{0.44}MnO_2$ cathode (made with hydrated $NaMnO_2$ (birnassite) as a binder) in aqueous Na_2SO_4 electrolyte. Figure 30B shows specific capacity versus cycle number for long term testing (over about 25 cycles) of a full aqueous Na-ion hybrid energy storage device based on a composite $Na_{0.44}MnO_2$ cathode (made with hydrated $NaMnO_2$ (birnassite) as a binder) in aqueous Na_2SO_4 electrolyte.

DETAILED DESCRIPTION OF THE INVENTION

[0040] Hybrid electrochemical energy storage systems of embodiments of the present invention include a double-layer capacitor electrode coupled with an active electrode. In these systems, the capacitor electrode stores charge through a reversible nonfaradiac reaction of Na cations on the surface of the electrode (double-layer), while the active electrode undergoes a reversible faradic reaction in a transition metal oxide that intercalates and deintercalates Na cations similar to that of a battery.

[0041] An example of a Li-based system has been described by Wang, et al., which utilizes a spinel structure $LiMn_2O_4$ battery electrode, an activated carbon capacitor electrode, and an aqueous Li_2SO_4 electrolyte. Wang, et al., Electrochemistry Communications, 7:1138-42 (2005). In this system, the negative anode electrode stores charge through a reversible nonfaradiac reaction of Li-ion on the surface of an activated carbon electrode. The positive cathode electrode utilizes a reversible faradiac reaction of Li-ion intercalation / deintercalation in spinel $LiMn_2O_4$.

[0042] In embodiments of the present invention, the charge / discharge processes of a device are associated with the transfer of Na cations between the active cathode electrode material and the anode electrode, with a Na cation containing electrolyte acting primarily as an ionic conductor between the two electrodes. That is, the cation concentration in the electrolyte stays relatively constant through a charge / discharge cycle. As the system is charged, cations in the electrolyte solution are adsorbed onto the surface of the anode material. At the same time, cations deintercalate from the active cathode material, thus keeping cation electrolyte concentration roughly constant through the charging process. Conversely, as the system is discharged, cations in the electrolyte solution intercalate into the active cathode material. At the same time, cations desorb from the surface of the anode material, thus keeping cation electrolyte concentration roughly constant through the discharge process. This process is shown schematically in Figure 1.

[0043] The highly-purified solvent-based non-aqueous electrolytes that must be used in energy storage devices, such as batteries, supercapacitors, or hybrid-energy storage systems, is a source of expense. Highly purified solvent-based non-aqueous electrolytes are typically necessary in Li-based systems because Li-ion systems are designed to have a relatively high operating potential, typically between about 3.3 and 4.2 V. Such high operating potentials are problematic for aqueous systems because water is electrolyzed at ~1.3 V, so non-aqueous (i.e., solvent-based) electrolytes that are stable to >4 V are needed. This results in several undesirable consequences. First, the conductivity of these solvent-based electrolytes is much lower than water-based electrolytes, so Li-ion batteries are either significantly rate limited, or must be fabricated in such a way that they have very thin porous electrodes. Usually the latter design is selected despite being a much more complicated design with high surface area current collectors, very thin roll-coated electrodes, and a large-area polymer separator. Much of the cost associated with state of the art Li-ion batteries is a result of this design paradigm. Second, the cost of handling and fabrication is elevated since a moisture-free environment must be maintained during battery assembly. Third, a controlled moisture-free fabrication environment is required, which also increases cost and complexity.

[0044] In contrast, embodiments of the present invention provide a secondary (rechargeable) energy storage system which uses a water-based (aqueous) electrolyte, such as a Na-based aqueous electrolyte. This allows for use of much thicker electrodes, much less expensive separator and current collector materials, and benign and more environmentally friendly materials for electrodes and electrolyte salts. Additionally, energy storage systems of embodiments of the present invention can be assembled in an open-air environment, resulting in a significantly lower cost of production.

[0045] Secondary (rechargeable) energy storage systems of embodiments of the present invention comprise an anode (i.e., negative) electrode, an anode side current collector, a cathode (i.e., positive) electrode, a cathode side current collector, a separator, and a Na-ion containing aqueous electrolyte. Any material capable of reversible intercalation / deintercalation of Na-ions may be used as an active cathode material. Any material capable of reversible adsorption / desorption of Na-ions and can function together with such an active cathode material and an appropriate electrolyte solution may be used as an anode material. As shown in the schematic of an exemplary device in Figure 2, the cathode side current collector **1** is in contact with the cathode electrode **3**. The cathode electrode **3** is in contact with the electrolyte solution **5**, which is also in contact with the anode electrode **9**. The separator **7** is located in the electrolyte solution **5** at a point between the cathode electrode **3** and the anode electrode **9**. The anode electrode is also in contact with the anode side current collector **11**. In Figure 2, the components of the exemplary device are shown as not being in contact with each other. The device was illustrated this way to clearly indicate the presence of the electrolyte solution relative to both electrodes. However, in actual embodiments, the cathode electrode **3** is in contact with the separator **7**, which is in contact with the anode electrode **9**.

Device Components

Cathode

[0046] Several materials comprising a transition metal oxide, sulfide, phosphate, or fluoride can be used as active cathode materials capable of reversible Na-ion intercalation / deintercalation. Materials suitable for use as active cathode materials in embodiments of the present invention preferably contain alkali atoms, such as sodium, lithium, or both, prior to use as active cathode materials. It is not necessary for an active cathode material to contain Na and/or Li in the as-formed state (that is, prior to use in an energy storage device). However, Na cations from the electrolyte must be able to incorporate into the active cathode material by intercalation during operation of the energy storage device. Thus, materials that may be used as cathodes in the present invention comprise materials that do not necessarily contain Na in an as-formed state, but are capable of reversible intercalation / deintercalation of Na-ions during discharging / charging cycles of the energy storage device without a large overpotential loss.

[0047] In embodiments where the active cathode material contains akali-atoms (preferably Na or Li) prior to use, some or all of these atoms are deintercalated during the first cell charging cycle. Alkali cations from the electrolyte (overwhelmingly Na cations) are re-intercalated during cell discharge. This is different than nearly all of the hybrid capacitor systems that call out an intercalation electrode opposite activated carbon. In most systems, cations from the electrolyte are adsorbed on the anode during a charging cycle. At the same time, the counter-anions, such as hydrogen ions, in the electrolyte intercalate into the active cathode material, thus preserving charge balance, but depleting ionic concentration, in the electrolyte solution. During discharge, cations are released from the anode and anions are released from the cathode, thus preserving charge balance, but increasing ionic concentration, in the electrolyte solution. This is a different operational mode from devices in embodiments of the present invention, where hydrogen ions or other anions are preferably not intercalated into the cathode active material.

[0048] Suitable active cathode materials may have the following general formula during use: $A_xM_yO_z$, where A is Na or a mixture of Na and one or more of Li, K, Be, Mg, and Ca, where x is within the range of 0 to 1, inclusive, before use and within the range of 0 to 10, inclusive, during use; M comprises any one or more transition metal, where y is within the range of 1 to 3, inclusive; preferably within the range of 1.5 and 2.5, inclusive; and O is oxygen, where z is within the range of 2 to 7, inclusive; preferably within the range of 3.5 to 4.5, inclusive.

[0049] In some active cathode materials with the general formula $A_xM_yO_z$, Na-ions reversibly intercalate / deintercalate during the discharge / charge cycle of the energy storage device. Thus, the quantity x in the active cathode material formula changes while the device is in use.

[0050] In some active cathode materials with the general formula $A_xM_yO_z$, A comprises at least 50 at% of at least one or more of Na, K, Be, Mg, or Ca, optionally in combination with Li; M comprises any one or more transition metal; O is oxygen; x ranges from 3.5 to 4.5 before use and from 1 to 10 during use; y ranges from 8.5 to 9.5 and z ranges from 17.5 to 18.5. In these embodiments, A preferably comprises at least 51 at% Na, such as at least 75 at% Na, and 0 to 49 at%, such as 0 to 25 at%, Li, K, Be, Mg, or Ca; M comprises one or more of Mn, Ti, Fe, Co, Ni, Cu, V, or Sc; x is about 4 before use and ranges from 0 to 10 during use; y is about 9; and z is about 18.

[0051] In some active cathode materials with the general formula $A_xM_yO_z$, A comprises Na or a mix of at least 80 atomic percent Na and one or more of Li, K, Be, Mg, and Ca. In these embodiments, x is preferably about 1 before use and ranges from 0 to about 1.5 during use. In some preferred active cathode materials, M comprises one or more of Mn, Ti, Fe, Co, Ni, Cu, and V, and may be doped (less than 20 at%, such as 0.1 to 10 at%; for example, 3 to 6 at%) with one or more of Al, Mg, Ga, In, Cu, Zn, and Ni.

[0052] General classes of suitable active cathode materials include (but are not limited to) the layered/orthorhombic $NaMO_2$ (birnessite), the cubic spinel based manganate (e.g., MO_2, such as λ-MnO_2 based material where M is Mn, e.g., $Li_xM_2O_4$ (where $1 \leq x < 1.1$) before use and $Na_yMn_2O_4$ in use), the $Na_2M_3O_7$ system, the $NaMPO_4$ system, the $NaM_2(PO_4)_3$ system, the Na_2MPO_4F system, and the tunnel-structured $Na_{0.44}MO_2$, where M in all formula comprises at least one transition metal. Typical transition metals may be Mn or Fe (for cost and environmental reasons), although Co, Ni, Cr, V, Ti, Cu, Zr, Nb, W, Mo (among others), or combinations thereof, may be used to wholly or partially replace Mn, Fe, or a combination thereof. In embodiments of the present invention, Mn is a preferred transition metal. In some embodiments, cathode electrodes may comprise multiple active cathode materials, either in a homogenous or near homogenous mixture or layered within the cathode electrode.

[0053] In some embodiments, the initial active cathode material comprises $NaMnO_2$ (birnassite structure) optionally doped with one or more metals, such as Li or Al.

[0054] In some embodiments, the initial active cathode material comprises λ-MnO_2 (i.e., the cubic isomorph of manganese oxide) based material, optionally doped with one or more metals, such as Li or Al.

[0055] In these embodiments, cubic spinel λ-MnO_2 may be formed by first forming a lithium containing manganese oxide, such as lithium manganate (e.g., cubic spinel $LiMn_2O_4$ or non-stoichiometric variants thereof). In embodiments which utilize a cubic spinel λ-MnO_2 active cathode material, most or all of the Li may be extracted electrochemically or chemically from the cubic spinel $LiMn_2O_4$ to form cubic spinel λ-MnO_2 type material (i.e., material which has a 1:2 Mn to O ratio, and/or in which the Mn may be substituted by another metal, and/or which also contains an alkali metal, and/or in which the Mn to O ratio is not exactly 1:2). This extraction may take place as part of the initial device charging cycle. In such instances, Li-ions are deintercalated from the as-formed cubic spinel $LiMn_2O_4$ during the first charging cycle. Upon discharge, Na-ions from the electrolyte intercalate into the cubic spinel λ-MnO_2. As such, the formula for the active cathode material during operation is $Na_yLi_xMn_2O_4$ (optionally doped with one or more additional metal as described above, preferably Al), with $0 < x < 1$, $0 < y < 1$, and $x + y \leq 1.1$. Preferably, the quantity x + y changes through the charge / discharge cycle from about 0 (fully charged) to about 1 (fully discharged). However, values above 1 during full discharge may be used. Furthermore, any other suitable formation method may be used. Non-stoichiometric $Li_xMn_2O_4$ materials with more than 1 Li for every 2 Mn and 4 O atoms may be used as initial materials from which cubic spinel λ-MnO_2 may be formed (where $1 \leq x < 1.1$ for example). Thus, the cubic spinel λ-manganate may have a formula $Al_zLi_xMn_{2-z}O_4$ where $1 \leq x < 1.1$ and $0 \leq z < 0.1$ before use, and $Al_zLi_xNa_yMn_2O_4$ where $0 \leq x < 1.1$, $0 \leq x < 1$, $0 \leq x+y < 1.1$, and $0 \leq z < 0.1$ in use (and where Al may be substituted by another dopant).

[0056] In some embodiments, the initial cathode material comprises $Na_2Mn_3O_7$, optionally doped with one or more metals, such as Li or Al.

[0057] In some embodiments, the initial cathode material comprises Na_2FePO_4F, optionally doped with one or more metals, such as Li or Al.

[0058] In some embodiments, the cathode material comprises $Na_{0.44}MnO_2$, optionally doped with one or more metals, such as Li or Al. This active cathode material may be made by thoroughly mixing Na_2CO_3 and Mn_2O_3 to proper molar ratios and firing, for example at about 800°C. The degree of Na content incorporated into this material during firing determines the oxidation state of the Mn and how it bonds with O_2 locally. This material has been demonstrated to cycle between $0.33 < x < 0.66$ for Na_xMnO_2 in a non-aqueous electrolyte.

[0059] Optionally, the cathode electrode may be in the form of a composite cathode comprising one or more active cathode materials, a high surface area conductive diluent (such as conducting grade graphite, carbon blacks, such as acetylene black, non-reactive metals, and/or conductive polymers), a binder, a plasticizer, and/or a filler. Exemplary binders may comprise polytetrafluoroethylene (PTFE), a polyvinylchloride (PVC)-based composite (including a PVC-SiO_2 composite), cellulose-based materials, polyvinylidene fluoride (PVDF), hydrated birnassite (when the active cathode material comprises another material), other non-reactive non-corroding polymer materials, or a combination thereof. A composite cathode may be formed by mixing a portion of one or more preferred active cathode materials with a conductive diluent, and/or a polymeric binder, and pressing the mixture into a pellet. In some embodiments, a composite cathode electrode may be formed from a mixture of about 50 to 90 wt% active cathode material, with the remainder of the mixture comprising a combination of one or more of diluent, binder, plasticizer, and/or filler. For example, in some embodiments, a composite cathode electrode may be formed from about 80 wt% active cathode material, about 10 to 15 wt% diluent, such as carbon black, and about 5 to 10 wt% binder, such as PTFE.

[0060] One or more additional functional materials may optionally be added to a composite cathode to increase capacity and replace the polymeric binder. These optional materials include but are not limited to Zn, Pb, hydrated $NaMnO_2$ (birnassite), and hydrated $Na_{0.44}MnO_2$ (orthorhombic tunnel structure). In instances where hydrated $NaMnO_2$ (birnassite) and/or hydrated $Na_{0.44}MnO_2$ (orthorhombic tunnel structure) is added to a composite cathode, the resulting device has a dual functional material composite cathode.

[0061] A cathode electrode will generally have a thickness in the range of about 40 to 800 μm.

Anode:

[0062] The anode may comprise any material capable of reversibly storing Na-ions through surface adsorption / desorption (via an electrochemical double layer reaction and/or a pseudocapacitive reaction (i.e., a i.e. partial charge transfer surface interaction)) and have sufficient capacity in the desired voltage range. Exemplary materials meeting these requirements include porous activated carbon, graphite, mesoporous carbon, carbon nanotubes, disordered carbon, Ti-oxide (such as titania) materials, V-oxide materials, phospho-olivine materials, other suitable mesoporous ceramic materials, and a combinations thereof. In preferred embodiments, activated carbon is used as the anode material.

[0063] Optionally, the anode electrode may be in the form of a composite anode comprising one or more anode materials, a high surface area conductive diluent (such as conducting grade graphite, carbon blacks, such as acetylene black, non-reactive metals, and/or conductive polymers), a binder, such as PTFE, a PVC-based composite (including a PVC-SiO_2 composite), cellulose-based materials, PVDF, other non-reactive non-corroding polymer materials, or a combination thereof, plasticizer, and/or a filler. A composite anode may be formed my mixing a portion of one or more preferred anode materials with a conductive diluent, and/or a polymeric binder, and pressing the mixture into a pellet. In some embodiments, a composite anode electrode may be formed from a mixture from about 50 to 90 wt% anode material, with the remainder of the mixture comprising a combination of one or more of diluent, binder, plasticizer, and/or filler. For example, in some embodiments, a composite cathode electrode may be formed from about 80 wt% activated carbon, about 10 to 15 wt% diluent, such as carbon black, and about 5 to 10 wt% binder, such as PTFE.

[0064] One or more additional functional materials may optionally be added to a composite anode to increase capacity and replace the polymeric binder. These optional materials include but are not limited to Zn, Pb, hydrated $NaMnO_2$ (birnassite), and hydrated $Na_{0.44}MnO_2$ (orthorhombic tunnel structure).

[0065] An anode electrode will generally have a thickness in the range of about 80 to 1600 μm.

Current Collectors:

[0066] In embodiments of the present invention, the cathode and anode materials may be mounted on current collectors. For optimal performance, current collectors are desirable that are electronically conductive and corrosion resistant in the electrolyte (aqueous Na-cation containing solutions, described below) at operational potentials.

[0067] For example, an anode current collector must be stable in a range of approximately -1.2 to -0.5 V vs. a standard Hg/Hg_2SO_4 reference electrode, since this is the nominal potential range that the anode half of the electrochemical cell is exposed during use. A cathode current collector must be stable in a range of approximately 0.1 to 0.7 V vs. a standard Hg/Hg_2SO_4 reference electrode.

[0068] Suitable uncoated current collector materials for the anode side include stainless steel, Ni, Ni-Cr alloys, Al, Ti, Cu, Pb and Pb alloys, refractory metals, and noble metals.

[0069] Suitable uncoated current collector materials for the cathode side include stainless steel, Ni, Ni-Cr alloys, Ti, Pb-oxides (PbO_x), and noble metals.

[0070] Current collectors may comprise solid foils or mesh materials.

[0071] Another approach is to coat a metal foil current collector of a suitable metal, such as Al, with a thin passivation layer that will not corrode and will protect the foil onto which it is deposited. Such corrosion resistant layers may be, but are not limited to, TiN, CrN, C, CN, NiZr, NiCr, Mo, Ti, Ta, Pt, Pd, Zr, W, FeN, CoN, etc. These coated current collectors may be used for the anode and/or cathode sides of a cell. In one embodiment, the cathode current collector comprises Al foil coated with TiN, FeN, C, or CN. The coating may be accomplished by any method known in the art, such as but not limited to physical vapor deposition such as sputtering, chemical vapor deposition, electrodeposition, spray deposition, or lamination.

Electrolyte:

[0072] Electrolytes useful in embodiments of the present invention comprise a salt dissolved fully in water. For example, the electrolyte may comprise a 0.1 M to 10 M solution of at least one anion selected from the group consisting of SO_4^{2-} , NO_3^-, ClO_4^-, PO_4^{3-}, CO_3^{2-}, Cl^-, and/or OH^-. Thus, Na cation containing salts may include (but are not limited to) Na_2SO_4, $NaNO_3$, $NaClO_4$, Na_3PO_4, Na_2CO_3, NaCl, and NaOH, or a combination thereof.

[0073] In some embodiments, the electrolyte solution may be substantially free of Na. In these instances, cations in salts of the above listed anions may be an alkali other than Na (such as K) or alkaline earth (such as Ca, or Mg) cation. Thus, alkali other than Na cation containing salts may include (but are not limited to) K_2SO_4, KNO_3, $KClO_4$, K_3PO_4, K_2CO_3, KCl, and KOH. Exemplary alkaline earth cation containing salts may include $CaSO_4$, $Ca(NO_3)_2$, $Ca(ClO_4)_2$, $CaCO_3$, and $Ca(OH)_2$, $MgSO_4$, $Mg(NO_3)_2$, $Mg(ClO_4)_2$, $MgCO_3$, and $Mg(OH)_2$. Electrolyte solutions substantially free of Na may be made from any combination of such salts. In other embodiments, the electrolyte solution may comprise a solution of a Na cation containing salt and one or more non-Na cation containing salt.

[0074] Molar concentrations preferably range from about 0.05 M to 3 M, such as about 0.1 to 1 M, at 100°C for Na_2SO_4 in water depending on the desired performance characteristics of the energy storage device, and the degradation / performance limiting mechanisms associated with higher salt concentrations. Similar ranges are preferred for other salts.

[0075] A blend of different salts (such as a blend of a sodium containing salt with one or more of an alkali, alkaline earth, lanthanide, aluminum and zinc salt) may result in an optimized system. Such a blend may provide an electrolyte with sodium cations and one or more cations selected from the group consisting of alkali (such as K), alkaline earth (such as Mg and Ca), lanthanide, aluminum, and zinc cations.

[0076] Optionally, the pH of the electrolyte may be altered by adding some additional OH^- ionic species to make the electrolyte solution more basic, for example by adding NaOH other OH-containing salts, or by adding some other

OH^- concentration-affecting compound (such as H_2SO_4 to make the electrolyte solution more acidic). The pH of the electrolyte affects the range of voltage stability window (relative to a reference electrode) of the cell and also can have an effect on the stability and degradation of the active cathode material and may inhibit proton (H^+) intercalation, which may play a role in active cathode material capacity loss and cell degradation. In some cases, the pH can be increased to 11 to 13, thereby allowing different active cathode materials to be stable (than were stable at neutral pH 7). In some embodiments, the pH may be within the range of about 3 to 13, such as between about 3 and 6 or between about 8 and 13.

[0077] Optionally, the electrolyte solution contains an additive for mitigating degradation of the active cathode material, such as birnassite material. An exemplary additive may be, but is not limited to, Na_2HPO_4, in quantities sufficient to establish a concentration ranging from 0.1 mM to 100 mM.

Separator:

[0078] A separator for use in embodiments of the present invention may comprise a cotton sheet, PVC (polyvinyl chloride), PE (polyethylene), glass fiber or any other suitable material.

Operational Characteristics

[0079] As described above, in embodiments where the active cathode material contains akali-atoms (preferably Na or Li) prior to use, some or all of these atoms are deintercalated during the first cell charging cycle. Alkali cations from the electrolyte (overwhelmingly Na cations) are re-intercalated during cell discharge. This is different than nearly all of the hybrid capacitor systems that call out an intercalation electrode opposite activated carbon. In most systems, cations from the electrolyte are adsorbed on the anode during a charging cycle. At the same time, the counter-anions in the electrolyte intercalate into the active cathode material, thus preserving charge balance, but depleting ionic concentration, in the electrolyte solution. During discharge, cations are released from the anode and anions are released from the cathode, thus preserving charge balance, but increasing ionic concentration, in the electrolyte solution. This is a different operational mode from devices in embodiments of the present invention.

[0080] In some embodiments, a hybrid energy storage device according to an embodiment of the present invention may be capable of operating over 500 cycles, such as over 5000 cycles, such as between 5000 and 10000 cycles at full discharge with less than 20% loss of initial capacity; preferably less than or equal to 10% loss of initial capacity; preferably less than or equal to about 5% loss of initial capacity, such as between 0 and 10 % loss of initial capacity; such as between 1 and 5 %.

[0081] In some embodiments, a hybrid energy storage device according to an embodiment of the present invention comprises an activated carbon anode material exhibiting greater than or equal to about 60 mAh/g specific capacity (cathode basis), such as 60 to 130 mAh/g (cathode basis), with Na_2SO_4 electrolyte.

[0082] In some embodiments, a hybrid energy storage device according to an embodiment of the present invention comprises a $Na_{0.44}MnO_2$–type active cathode material exhibiting greater than or equal to about 20 mAh/g specific capacity with Na_2SO_4 electrolyte, such as about 45 to 80 mAh/g (cathode basis).

[0083] In some embodiments, a hybrid energy storage device according to an embodiment of the present invention comprises a $Na_{0.44}MO_2$–type active cathode material, an activated carbon anode material, and exhibits a specific energy (normalized to active cathode and anode material mass) of greater than 20 Wh/kg, such as between 20 and 35 Wh/kg, when cycled between potentials of 0.35 and 1.5 V in 1 M Na_2SO_4 at C/5 rate or slower.

[0084] In some embodiments, a hybrid energy storage device according to an embodiment of the present invention comprises a cubic spinel λ-MO_2-NaM_2O_4-type active cathode material exhibiting greater than or equal to about 75 mAh/g specific capacity (cathode basis) with Na_2SO_4 electrolyte.

[0085] In some embodiments, a hybrid energy storage device according to an embodiment of the present invention comprises a cubic spinel λ-MO_2-NaM_2O_4-type active cathode material, an activated carbon anode material, and exhibits a specific energy (normalized to active cathode and anode material mass) of greater than 20 Wh/kg, such as between about 20 and 105 Wh/kg (when cycled between potentials of 0.60 and 1.55 V in 1 M Na_2SO_4 at C/10 rate or slower); preferably as greater than 40 Wh/kg, such as between 40 and 105 Wh/kg (when cycled between potentials of 0.60 and 1.9 V in 1 M Na_2SO_4 at C/10 rate or slower).

[0086] In some embodiments, a hybrid energy storage device according to an embodiment of the present invention comprises a cubic spinel λ-MO_2-NaM_2O_4-type active cathode material, an activated carbon anode material, and exhibits a specific energy (normalized to active cathode and anode material mass) of between 10 and 105 Wh/kg (cathode basis), for a specific power of between 20 to 1100 W/kg, such as between about 70 and about 105 Wh/kg for between 20 and 100 W/kg, at 23°C at 0.1C rate.

[0087] In some embodiments, a hybrid energy storage device according to an embodiment of the present invention comprises a cubic spinel λ-MO_2-NaM_2O_4-type active cathode material, an activated carbon anode material, and exhibits a specific energy (normalized to active cathode and anode material mass) of between 30 and 50 Wh/kg, at -5 to 23°C at 1 C rate. In some embodiments, the specific energy is between 65 and 100 Wh/kg, at -5 to 23°C at 0.5 C rate.

[0088] In some embodiments, a hybrid energy storage device according to an embodiment of the present invention comprises a cathode electrode that is able to support greater than 1 kW of discharge power per kg of active cathode material. In these embodiments, the active cathode material may comprise $Na_{0.44}MnO_2$ or λ-$NaMnO_2$ (cubic spinel $NaMn_2O_4$)

[0089] The following examples serve to illustrate the invention. These Examples are in no way intended to limit the scope of the claimed methods and devices.

EXAMPLES

Example 1

[0090] A test cell was constructed with a λ-MO_2–type active cathode material versus an activated carbon anode material in 1 M Na_2SO_4 in DI H_2O electrolyte.

[0091] The active cathode material was made from Al-doped, Li-containing, cubic spinel MnO_2. Specifically, the Li-containing cubic spinel was synthesized by thoroughly mixing Li_2CO_3, Mn_2O_3, and $Al(OH)_3$ to proper mole ratios and firing at 750°C for 24 hours. This material resulted in a spinel structure with the formula $Li_{1.05}Mn_{1.89}Al_{0.06}O_4$, as verified by X-ray diffraction analysis. X-ray spectra is shown in Figure 3. As the X-ray data confirm, this material fits the well known cubic spinel $LiMn_2O_4$ structure, as archived by JCPDS card # 00-035-0782.

[0092] A composite cathode was formed by mixing about 80 wt% $Li_{1.05}Mn_{1.89}Al_{0.06}O_4$ initial active material, 10 wt% carbon black conductive diluent, and about 10% PTFE polymeric binder. This mixture was then pressed into a pellet, which was placed into a large electrochemical cell and biased to remove most of the Li. The cell was held at greater than 4.1 V for at least 5 hours to electrochemically extract the Li, although chemical extraction could have been used instead.

[0093] Once the electrochemical extraction was completed, X-ray diffraction analysis was again performed on the pellet, and a new Al-doped λ-MnO_2 phase was indicated that was substantially free of Li (i.e., 0 to 5 at% Li may have remained). The diffraction pattern from the new phase is shown in Figure 3.

[0094] The data in Figure 4 show that the material is a close match to λ-MnO_2 as described by JCPDS card # 00-044-0992. The diffraction patterns shown in Figures 3 and 4 are superimposed in Figure 5 to demonstrate the difference.

[0095] The resulting Al-doped λ-MnO_2 material was then placed as a working electrode (cathode) into an electrochemical half cell environment with a Pt counter electrode, and a mercury /mercury sulfate reference electrode, and a Na_2SO_4 aqueous electrolyte. The half-cell was cycled between -0.3 and 0.6 V vs. SME. The data indicate that the cathode does display Na-ion intercalation / deintercalation events and is stable over many cycles. The data shown in Figure 6 show three sequential cyclic voltammargrams obtained after ten conditioning cycles. This result indicates that Al-doped λ-MnO_2 is able to reversibly intercalate Na cations from a Na cation containing electrolyte with virtually no Li or Li cations present.

[0096] To make a functional cell, a pellet was pressed of the composite Li-containing active cathode material described above and placed in a coin cell. The anode, separator, and electrolyte in the coin cell are described below.

[0097] Activated carbon was used as the anode material. This material is known to reversibly store Li cations through surface adsorption / desorption and also has sufficient capacity in the desired voltage range. It was anticipated that this material could store between 40 and 100 mAh/g of Na^+ in the voltage range of 1.5 to 2 V vs. Na metal.

[0098] A composite anode was formed by mixing about 80 wt% activated carbon, 10 wt% carbon black conductive diluent, and 10 wt% PTFE polymeric binder and pressing the mixture into a pellet. The density of the pellet was at least 0.35 g/cm^3. The mass of the pressed anode pellet was matched to the mass of the cathode pellet so that both electrodes could hold sufficient Na cations to make maximum use of the active material present.

[0099] This composite anode material was placed as a working electrode into an electrochemical half cell environment with a Pt counter electrode, and a mercury /mercury sulfate reference electrode. The half-cell was cycled between -0.6 and 0.7 V vs. SME, with a 1 M Na_2SO_4 electrolyte solution. The data indicate that the anode material does not display Na-ion intercalation / deintercalation events, exhibited symmetrical behavior indicative of a reversible Na cation storage process via a surface adsorption / electrochemical double layer capacitance effect. A cyclic voltammargram obtained from this half cell is shown in Figure 7.

[00100] The anode and cathode material pellets were fitted into standard stainless steel 2032 coin cell test fixtures. Cotton sheeting was used as a separator material, and Ni mesh served a current collectors for both electrodes. After some irreversible capacity loss on the first several formation cycles, typical charge/discharge behavior was observed to be very consistent and stable in the voltage range between 0.8 and 1.8 V, at least, as shown in Figure 8. The cell delivered uniform charge / discharge behavior during both C/24 and 2 C cycling and little obvious decay was observed.

[00101] Data showing a single C/5 discharge curve as a function of time and as a function of specific energy are shown in Figures 9A and 9B, respectively. Data showing a single C/10 discharge curve as a function of specific energy is shown in Figure 10.

[00102] Further study indicated that the cells are stable and can be cycled repeatedly between 1.8 and 0.8 V, at least. The cells also exhibit excellent long-term stability. Figures 12A and 12B show specific energy and specific capacity, respectively, versus cycle number for long term testing (up to 40 cycles). After the formation cycling is complete, a near-100% columbic efficiency is observed. Figure 12C shows extended high rate cycling performance, with little cell capacity degradation observed over 570 cycles at 5°C. As seen in Figure 17, such cells exhibit little to no degradation for 1000 or more charge / discharge cycles and less than 10% degradation over 5000 or more cycles, such as 5000 to 10,000 cycles.

[00103] Figure 13 shows the energy density of such cells as a function of cycle number, Figure 14 shows the specific energy versus discharge rate, and Figure 15 shows the specific energy versus specific power. Finally, temperature dependency studies were conducted. Figure 16 shows the temperature dependency of the specific energy versus discharge rates for a cell with this active cathode material.

[00104] Additionally, a large scale cell (i.e., a two cell stack) was constructed with the active cathode material composite electrode versus an activated carbon anode electrode. The cell potential versus the cell energy is shown in Figure 18.

[00105] A separate test cell was constructed from a fully de-lithiated, Al doped cubic spinel active cathode material (where Li was removed in a half cell environment described above and replaced with Na electrochemically in a half cell before assembling in the test cell) to demonstrate that this material is fully functional as an active cathode material. Cell cycle characteristics for this cell are shown in Figures 11A and 11B. The cell showed significant capacity and a similar characteristic charge discharge profile as the cell where the starting material was Al doped $LiMn_2O_4$, described above.

[00106] In the processing of the above active cathode material, Li could have been removed chemically with a Br containing solution followed by washing. Additionally, Na could have also been added to a de-lithiated, cubic spinel active cathode material chemically by treatment with molten Na salt or Na containing solution.

Example 2

[00107] A test cell similar to that described in Example 1 above was constructed with a $NaMnO_2$ (birnassite structure) active cathode material, activated carbon anode material, and 1 M Na_2SO_4 in DI H_2O electrolyte.

[00108] Figure 19 shows the charge / discharge behavior (i.e., cell potential versus time through charge / discharge cycles) of the $NaMnO_2$ (birnassite phase) active cathode material test cell. The system demonstrated a potential range of about 0.0 V to about 1.7 V.

Example 3

[00109] A half cell similar to that described in Example 1 above was constructed with a $Na_2Mn_3O_7$ (JCPDS structure: 078-0193) working electrode, a SCE reference electrode, and a Pt counter electrode. The half-cell was cycled between about -0.5 and 0.6 V vs. SCE. The data indicate that $Na_2Mn_3O_7$ does display Na cation intercalation / deintercalation events and is stable between the potential range studied. The data shown in Figure 20A show cyclic voltammargrams which demonstrate reversible capacity for $Na_2Mn_3O_7$ in 1 M Na_2SO_4 in DI H_2O electrolyte solution. Figure 20B shows a potential versus time profile from a portion of the same test.

[00110] Results of these studies indicate that $Na_2Mn_3O_7$ is a suitable active cathode material for use in embodiments of the present invention.

Example 4

[00111] A test cell similar to that described in Example 1 above was constructed with a Na_2FePO_4F active cathode material, activated carbon anode material, and 1 M Na_2SO_4 in DI H_2O electrolyte. Figure 21 shows the discharge behavior of the test cell over time. As seen in Figure 21, significant capacity was observed at about 0.8 V.

Example 5

[00112] A test cell and a half cell similar to those described in Example 1 were constructed with $Na_{0.44}MnO_2$ active cathode material. The $Na_{0.44}MnO_2$ active cathode material was as synthesized by thoroughly mixing Na_2CO_3 and Mn_2O_3 to proper molar ratios and firing at 800°C for 12 hours. The degree of Na content during firing determines the oxidation state of the Mn and how it bonds with O_2 locally. This material is known to cycle between $0.33 < x < 0.66$ for Na_xMnO_2 in a Na cation containing non-aqueous electrolyte. The specific capacity of this material is as much as 160 mAh/g in an organic electrolyte, with a voltage of 2 to 3 V vs. Na metal. A structural representation of the crystal structure is shown in Figure 22.

[00113] A composite cathode was formed according to a similar procedure as outlined in Example 1. In this case, 80 wt% $Na_{0.44}MnO_2$, 15 wt% carbon black conductive diluent, and 5 wt% PTFE polymeric binder were mixed and pressed into a pellet. The redox potential associated with Na-ion intercalation / deintercalation is below the breakdown potential (oxygen reduction) of water, demonstrating that the material is suitable for use with an aqueous electrolyte.

[00114] Activated carbon was used as the anode material. This material is known to reversibly store Li cations through surface adsorption / desorption and have sufficient capacity in the desired voltage range. It was anticipated that this material could store between 40 and 100 mAh/g of Na^+ in the voltage range of 1.5 to 2 V vs. Na metal.

[00115] A composite anode was formed according to a similar procedure as outlined in Example 1. In this case, 80 wt% activated carbon, 15 wt% carbon black conductive diluent, and 5 wt% PTFE polymeric binder were mixed and pressed into a pellet.

[00116] The electrolyte for the half cell was 2 N Na_2SO_4 in DI H_2O, and for the test cell was 1.5 M Na_2SO_4 in DI H_2O. Other work has shown that the same effect is present in salt concentrations ranging from 0.05 to 5 M.

[00117] The reversible nature of the $Na_{0.44}MnO_2$ active cathode material was examined using a three electrode half-cell set-up, with the pressed composite $Na_{0.44}MnO_2$ electrode affixed to Ni mesh and immersed into an open beaker of electrolyte. A standard sulfur-mercury electrode was used (Koslow scientific) as a reference electrode, and Pt wire as a counter electrode.

[00118] As can be seen in the cyclic voltammogram shown in Figure 23, the secondary nature of the material is evident, as is a capacitive element likely due to surface area effects related to the carbon black used when fabricating the composite $Na_{0.44}MnO_2$ electrode. There are four distinct reduction-oxidation peaks evident for this material. The symmetrical nature of this material is indicative of the fact that Na is inserted (under negative current conditions) and extracted (under positive current conditions) in a repeatable fashion.

[00119] A similar half-cell test was conducted for an activated carbon electrode in 2 N Na_2SO_4 in DI H_2O electrolyte solution. The cyclic voltammogram derived from this electrode demonstrate that there are no distinct oxidation-reduction peaks in aqueous Na_2SO_4 solution; however, symmetrical behavior was observed above about -0.6 V versus SME. This is indicative of a reversible Na cation storage process via surface adsorption. At voltages below -0.6 V, tailing was observed due to hydrogen evolution. The data is shown in Figure 24.

[00120] These two half-cell tests verify that the anode and cathode materials are functional in the desired aqueous environment and should be compatible with each other, as long as the cell is not over charged or over discharged, at which point water electrolysis would occur.

[00121] A series of the full cells similar to those described in Example 1 was then made and tested for a composite $Na_{0.44}MnO_2$ cathode, composite activated carbon anode, and aqueous Na_2SO_4 electrolyte. After some irreversible capacity loss on the formation cycle(s), typical charge/discharge behavior was very consistent and was stable in the voltage range between 0.35 and 1.8 V, at least, as seen in Figure 25. The cells demonstrated little obvious decay over about 15 hours.

[00122] Though the system under observation was not optimized, over 20 mAh/g (from the cathode) were delivered over many cycles. It is believed that this value may be significantly increased by optimizing composite electrode structure. A typical discharge curve is shown in Figure 26. A specific capacity between 15 and 36 mAh/g was observed for between 1.0 and 0.4 V cell potential. Further study indicated that the cells are stable and can be cycled repeatedly to 1.8 V, at least. The cells also exhibit excellent long-term stability. Figure 27 shows a portion of a long-duration cycle-life test. The cycle life behavior of this cell shows that there was no degradation over at least 180 cycles (over at least 40 continuous hours of testing) between 0.4 and 1.6 V cell potential. Charge and discharge capacity under about a 2C charge / discharge rate (at 2 mA charge / discharge and from 1.6 to 0.6 V potential window) are shown as a function of cycle in Figure 28. In these tests, columbic efficiency was observed to be greater than 90% even at these high current rates.

[00123] The charge and discharge energy of these cells is shown in Figure 29 as a function of cycle index. Minimal system fade was observed over the first 180 cycles, and even at a rate of greater than 2 C, the cell delivered a roundtrip energy efficiency of over 85% (about 87%). Efficiency would increase significantly at lower rates of charge / discharge, because nearly all efficiency loss is due to overpotential loss at higher currents.

Example 6

[00124] Another test cell similar to that described in Example 1 was constructed with $Na_{0.44}MnO_2$ active cathode material and hydrated $NaMnO_2$ (birnassite) as a binder material. The $Na_{0.44}MnO_2$ active cathode material was synthesized as described in Example 5.

[00125] The composite cathode was formed according to a similar procedure as outlined in Example 1. In this case, 80 wt% $Na_{0.44}MnO_2$, 15 wt% carbon black conductive diluent, and 5 wt% hydrated $NaMnO_2$ (birnassite) binder were mixed and pressed into a pellet.

[00126] Performance data of this test cell is shown in Figures 30A and 30B. Specifically, Figure 30A shows a plot of the cell potential versus specific capacity, and Figure 30B shows the capacity versus cycle number for long term testing (over about 25 cycles).

[00127] The foregoing description of the invention has been presented for purposes of illustration and description. The methods and devices illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms “comprising”, “including,” containing”, etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the invention embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention. It is intended that the scope of the invention be defined by the claims appended hereto, and their equivalents. All references described here are incorporated herein in their entirety.

What is claimed is:

1. A secondary hybrid aqueous energy storage device, comprising: an anode electrode, a cathode electrode which is capable of reversibly intercalating sodium cations, a separator, and a sodium cation containing aqueous electrolyte, wherein an initial active cathode electrode material in the device comprises an alkali metal containing active cathode electrode material which deintercalates alkali metal ions during initial charging of the device.

2. The device of claim 1, wherein the anode electrode comprises a double-layer capacitor electrode which stores charge through a reversible nonfaradiac reaction of alkali metal cations on a surface of the anode electrode or a pseudocapacitive electrode which undergoes a partial charge transfer surface interaction with alkali metal cations on a surface of the anode electrode.

3. The device of claim 1, wherein the initial active cathode electrode material comprises a transition metal oxide, sulfide, phosphate or fluoride.

4. The device of claim 3, wherein the initial active cathode electrode material comprises a transition metal oxide.

5. The device of claim 4, wherein the active cathode electrode material comprises a doped or undoped cubic spinel λ-MnO_2-type material.

6. The device of claim 5, wherein the doped or undoped cubic spinel λ-MnO_2-type material is formed by providing a lithium manganate cubic spinel material and then removing at least a portion of the lithium during the initial charging to form the λ-MnO_2-type material.

7. The device of claim 5, wherein the doped or undoped cubic spinel λ-MnO_2-type material is formed by providing a lithium manganate cubic spinel material, chemically or electrochemically removing at least a portion of the

lithium, and performing a chemical or electrochemical ion exchange to insert sodium into alkali metal sites of the λ-MnO_2-type material.

8. The device of claim 5, wherein the doped or undoped cubic spinel λ-MnO_2-type material comprises Al-doped cubic spinel λ-MnO_2.

9. The device of claim 5, wherein the doped or undoped cubic spinel λ-MnO_2-type material comprises Al-doped, and at least one of lithium, sodium, potassium, calcium, or magnesium containing cubic spinel λ-MnO_2.

10. The device of claim 3, wherein the initial active cathode electrode material comprises a doped or undoped layered orthorhombic $NaMnO_2$ birnessite material.

11. The device of claim 3 wherein the initial active cathode electrode material comprises a $Na_2M_3O_7$ material, wherein M comprises at least one transition metal.

12. The device of claim 3, wherein the initial active cathode electrode material comprises a doped or undoped $NaMPO_4$ material, wherein M comprises at least one transition metal.

13. The device of claim 3, wherein the initial active cathode electrode material comprises a doped or undoped $NaM_2(PO_4)_3$ material, wherein M comprises at least one transition metal.

14. The device of claim 3, wherein the initial active cathode electrode material comprises a doped or undoped Na_2MPO_4F material, wherein M comprises at least one transition metal.

15. The device of claim 3, wherein the initial active cathode electrode material comprises a doped or undoped tunnel-structured $Na_{0.44}MO_2$ material, wherein M comprises at least one transition metal.

16. The device of claim 3, wherein the transition metal is one or more transition metals selected from the group consisting of Mn, Fe, Co, Ni, Cr, V, Ti, Cu, Zr, Nb, W, and Mo.

17. The device of claim 3, wherein the anode comprises porous activated carbon, graphite, mesoporous carbon, carbon nanotubes, disordered carbon, Ti-oxide material, V-oxide material, phospho-olivine material, mesoporous ceramic material, or a composite thereof.

18. The device of claim 17, wherein the electrolyte comprises Na_2SO_4, $NaNO_3$, $NaClO_4$, Na_3PO_4, Na_2CO_3, NaCl, NaOH, or combination thereof.

19. The device of claim 17, wherein the electrolyte solution further comprises one or more salts comprising potassium, calcium, or magnesium.

20. The device of claim 1, further comprising a cathode current collector which comprises a Ni mesh, a coated Al foil, Ti, or stainless steel, and an anode current collector which comprises a Ni mesh, an Al foil, Ti, or stainless steel.

21. The device of claim 1, wherein the electrolyte comprises a sodium containing salt with potassium, calcium, or magnesium containing salt or combination thereof solvated in water, and initially excludes lithium ions.

22. The device of claim 1, wherein the electrolyte comprises Na_2SO_4 solvated in water, and initially excludes lithium ions.

23. The device of claim 3, wherein the active cathode electrode material has a formula $A_xM_yO_z$, where A is Na or a mixture of Na and one or more of Li, K, Be, Mg, and Ca, x is within a range of 0 to 1.1, inclusive, before use and within a range of 0 to 10, inclusive, during use; M comprises any one or more transition metal, y is within a range of 1 to 3, inclusive, O is oxygen, and z is within a range of 2 to 7, inclusive.

24. The device of claim 23, wherein y is within a range of 1.5 and 2.5, inclusive, and z is within a range of 3.5 to 4.5, inclusive.

25. The device of claim 24, wherein the active cathode electrode material comprises a cubic spinel λ-manganate having a formula $Li_xMn_{2-z}Al_zO_4$ where $1 \leq x < 1.1$ and $0 \leq z < 0.1$ before use, and $Li_xNa_yMn_{2-z}Al_zO_4$ where $0 \leq x < 1.1$, $0 \leq y < 1$, $0 \leq x+y < 1.1$, and $0 \leq z < 0.1$ in use.

26. The device of claim 25, wherein the active cathode material electrode exhibits greater than or equal to about 75 mAh/g specific capacity with Na_2SO_4 electrolyte.

27. The device of claim 26, wherein the device exhibits a specific energy of greater than 20 Wh per kg of active cathode material when cycled between potentials of 0.60 and 1.9 V in 1 M Na_2SO_4 at C/10 rate or slower.

28. The device of claim 26, wherein the device comprises an activated carbon anode material, and exhibits a specific energy of between 10 and 105 Wh per kg of active cathode material for a specific power of between 20 to 1000 W per kg of active cathode material at 23°C at 0.1C rate.

29. The device of claim 28, wherein the active cathode material exhibits a specific energy of between 30 and 50 Wh/kg at -5 to 23°C at 1 C rate.

30. The device of claim 3, wherein said active cathode electrode material has a formula $A_xM_yO_z$, where A comprises at least 50 at% Na; M comprises any one or more transition metal; O is oxygen; x ranges from 3.5 to 4.5 before use and from 1 to 10 during use; y ranges from 8.5 to 9.5 and z ranges from 17.5 to 18.5.

31. A method of operating hybrid aqueous energy storage device comprising an anode electrode, a cathode electrode, a separator, and a sodium containing aqueous electrolyte, the method comprising deintercalating alkali ions from an active cathode electrode material during initial charging of the device,

reversibly intercalating sodium ions into the active cathode electrode material during discharge cycles, and deintercalating sodium ions from the active cathode electrode during subsequent charge cycles.

32. The method of claim 31, wherein a cation concentration of the electrolyte is substantially constant during the discharge and charge cycles of the device.

33. The method of claim 31, wherein the active cathode electrode material comprises a transition metal oxide, sulfide, phosphate, or fluoride.

34. The method of claim 33, wherein the active cathode electrode material has a formula $A_xM_yO_z$, where A comprises Na, M comprises any one or more transition metal; O is oxygen; x ranges from 0 to 1 before use and from 0 to 10 during use; y ranges from 1.5 to 2.5, and z ranges from 3.5 to 4.5.

35. The method of claim 34, wherein A comprises Na during use and Li before the initial charging of the device and the active cathode electrode material is formed by providing lithium manganate cubic spinel material and then removing at least a portion of the lithium during the initial charging of the device to form a cubic spinel λ-manganate material.

36. The method of claim 35, wherein the cubic spinel λ-manganate has a formula $Li_xMn_{2-z}Al_zO_4$ where $1 \leq x < 1.1$ and $0 \leq z < 0.1$ before use, and $Li_xNa_yMn_{2-z}Al_zO_4$ where $0 \leq x < 1.1$, $0 \leq x < 1$, $0 \leq x+y < 1.1$, and $0 \leq z < 0.1$ in use.

37. The method of claim 36, wherein the device exhibits a specific energy of greater than 20 Wh per kg of active cathode material when cycled between potentials of 0.60 and 1.9 V in 1 M Na_2SO_4 at C/10 rate or slower.

38. The method of claim 36, wherein the device comprises an activated carbon anode material, and exhibits a specific energy of between 10 and 105 Wh

per kg of active cathode material for a specific power of between 20 to 1000 W per kg of active cathode material at 23°C at 0.1C rate.

39. The method of claim 38, wherein the device exhibits a specific energy of between 40 and 60 Wh per kg of active cathode material at -5 to 23°C at 1 C rate.

40. The method of claim 36, wherein the device exhibits greater than or equal to about 75 mAh per gram of active cathode material specific capacity with Na_2SO_4 electrolyte.

41. The method of claim 34, wherein the anode electrode comprises porous activated carbon, graphite, mesoporous carbon, carbon nanotubes, disordered carbon, Ti-oxide material, V-oxide material, phospho-olivine material, mesoporous ceramic material or a composite thereof, and the electrolyte comprises Na_2SO_4, $NaNO_3$, $NaClO_4$, Na_3PO_4, Na_2CO_3, NaCl, NaOH, or combination thereof.

42. The method of claim 31, wherein a charge containing electrochemical double layer is formed near the surface of an anode electrode during device charging, and the active charged species in this electrochemical double layer comprises Na ions, K ions, Ca ions, Li ions, or a combination thereof.

43. The method of claim 31, wherein a partial charge transfer interaction occurs near the surface of a pseudocapacitive anode electrode during device charging, and the active charged species in this partial charge transfer interaction comprises Na ions, K ions, Ca ions, Li ions, or a combination thereof.

44. The method of claim 31, wherein the active cathode electrode material does not intercalate or deintercalate electrolyte anions during the discharge and charge cycles.

45. The method of claim 43, wherein the active cathode material only reversibly intercalates and deintercalates alkali cations and does not intercalate and deintercalate protons during the discharge and charge cycles.

46. The method of claim 31, wherein the hybrid energy storage device operates between 5000 and 10000 cycles at full discharge with less than 20% loss of initial capacity.

47. The method of claim 31, wherein the hybrid energy storage device comprises a $Na_{0.44}MnO_2$–type active cathode material exhibiting greater than or equal to about 20 mAh per gram of active cathode material specific capacity with a Na_2SO_4 electrolyte.

48. The method of claim 31, wherein the hybrid energy storage device comprises a $Na_{0.44}MnO_2$–type active cathode material, an activated carbon anode material, and exhibits a specific energy of greater than 20 Wh per kg active cathode material when cycled between potentials of 0.35 and 1.5 V in 1 M Na_2SO_4 at C/5 rate or slower.

49. The method of claim 31, wherein the hybrid energy storage device comprises a cathode electrode comprising doped or undoped $Na_{0.44}MnO_2$ or λ-MnO_2 type active cathode material that supports greater than 1 kW of discharge power per kg of active cathode material.

50. A secondary hybrid aqueous energy storage device comprising an anode electrode, a cathode electrode which is capable of reversibly intercalating at least one of sodium, potassium, calcium, or magnesium cations, a separator, and an aqueous electrolyte that comprises at least one of sodium, potassium, calcium, or magnesium cations, wherein the active cathode electrode material comprises a cubic spinel λ-manganate.

51. The device of claim 50, wherein the cubic spinel λ-manganate has a formula $Li_xMn_{2-z}Al_zO_4$ where $1 \leq x < 1.1$ and $0 \leq z < 0.1$ before use, and

$Li_xNa_yMn_{2-z}Al_zO_4$ where $0 \leq x < 1.1$, $0 \leq x < 1$, $0 \leq x+y < 1.1$, and $0 \leq z < 0.1$ in use, and in use the cubic spinel λ-manganate reversibly intercalates at least one of sodium, potassium, calcium, or magnesium cations.

52. The device of claim 51, wherein the active cathode electrode material is formed by providing a lithium manganate cubic spinel material and then removing at least a portion of the lithium during an initial charging of the device to form the cubic spinel λ-manganate material.

53. The device of claim 51, wherein the anode electrode comprises a double-layer capacitor electrode which stores charge through a reversible nonfaradiac reaction of alkali metal cations on a surface of the anode electrode.

54. The device of claim 53, wherein the anode electrode comprises porous activated carbon, graphite, mesoporous carbon, carbon nanotubes, disordered carbon, Ti-oxide material, V-oxide material, phospho-olivine material, mesoporous ceramic material, or a composite thereof, and the electrolyte comprises Na_2SO_4, $NaNO_3$, $NaClO_4$, Na_3PO_4, Na_2CO_3, NaCl, NaOH, or combination thereof.

55. The device of claim 50, wherein the anode electrode comprises porous activated carbon, the electrolyte comprises Na_2SO_4, the cathode electrode contacts a cathode current collector and the anode electrode contacts an anode current collector.

56. The device of claim 50, wherein the cathode electrode comprises 80 to 90 % active cathode material, 0 to 10% conductive additive, and 0 to 10 % binder material, and the anode electrode comprises 80 to 90 % active anode material, 0 to 10% conductive additive, and 0 to 10 % binder material.

57. The device of claim 56, wherein the conductive additive comprises one or more of carbon black, graphite, a non-reactive metal, and a conductive polymer, and the binder comprises one or more of PTFE, PVC, cellulose-based material, PVDF, or other non-reactive non-corroding polymer material.

58. The device of claim 56, wherein the binder material for one or more of the cathode electrode and anode electrode comprises hydrated birnessite.

59. A method of making a secondary hybrid aqueous energy storage device, comprising:

providing the energy storage device comprising an anode electrode, a cathode electrode which is capable of reversibly intercalating sodium cations, a separator, and a sodium cation containing aqueous electrolyte, wherein the active cathode electrode material comprises a cubic spinel lithium manganate; and

removing at least a portion of the lithium during an initial charging of the device to form a cubic spinel λ-manganate active cathode electrode material.

60. The method of claim 59, wherein the anode electrode comprises a double-layer capacitor electrode which stores charge through a reversible nonfaradiac reaction of alkali metal cations on a surface of the anode electrode.

61. The method of claim 60, wherein:

the cubic spinel λ-manganate has a formula $Li_xMn_{2-z}Al_zO_4$ where $1 \leq x < 1.1$ and $0 \leq z < 0.1$ before use, and $Li_xNa_yMn_{2-z}Al_zO_4$ where $0 \leq x < 1.1$, $0 \leq x < 1$, $0 \leq x+y < 1.1$, and $0 \leq z < 0.1$ in use;

the anode electrode comprises porous activated carbon, graphite, mesoporous carbon, carbon nanotubes, disordered carbon, Ti-oxide material, V-oxide material, phospho-olivine material, mesoporous ceramic material, or a composite thereof; and

the electrolyte comprises Na_2SO_4, $NaNO_3$, $NaClO_4$, Na_3PO_4, Na_2CO_3, NaCl, NaOH, or combination thereof.

62. The method of claim 61, wherein the anode electrode comprises porous activated carbon, the electrolyte comprises Na_2SO_4, the cathode

electrode contacts a cathode current collector and the anode electrode contacts an anode current collector.

63. A secondary hybrid aqueous energy storage device, comprising: an anode electrode, a cathode electrode which is capable of reversibly intercalating potassium, calcium, or magnesium cations, a separator, and a potassium, calcium, or magnesium cation containing aqueous electrolyte, wherein an initial active cathode electrode material in the device comprises alkali containing active cathode electrode material which deintercalates alkali metal ions during initial charging of the device.

Figure 1

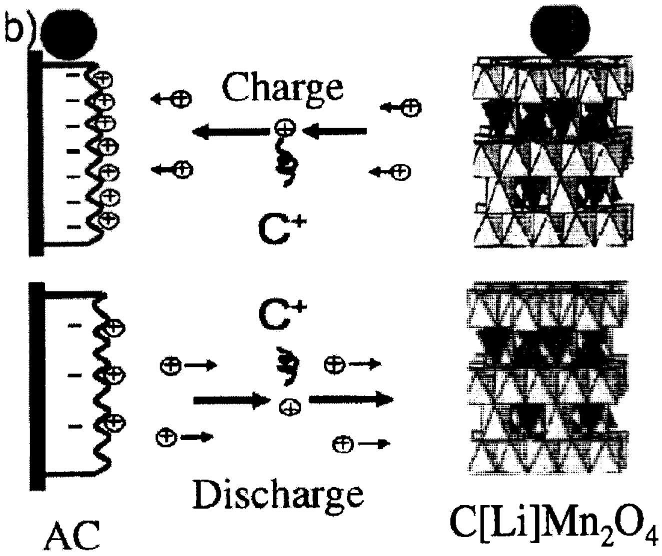


Figure 2

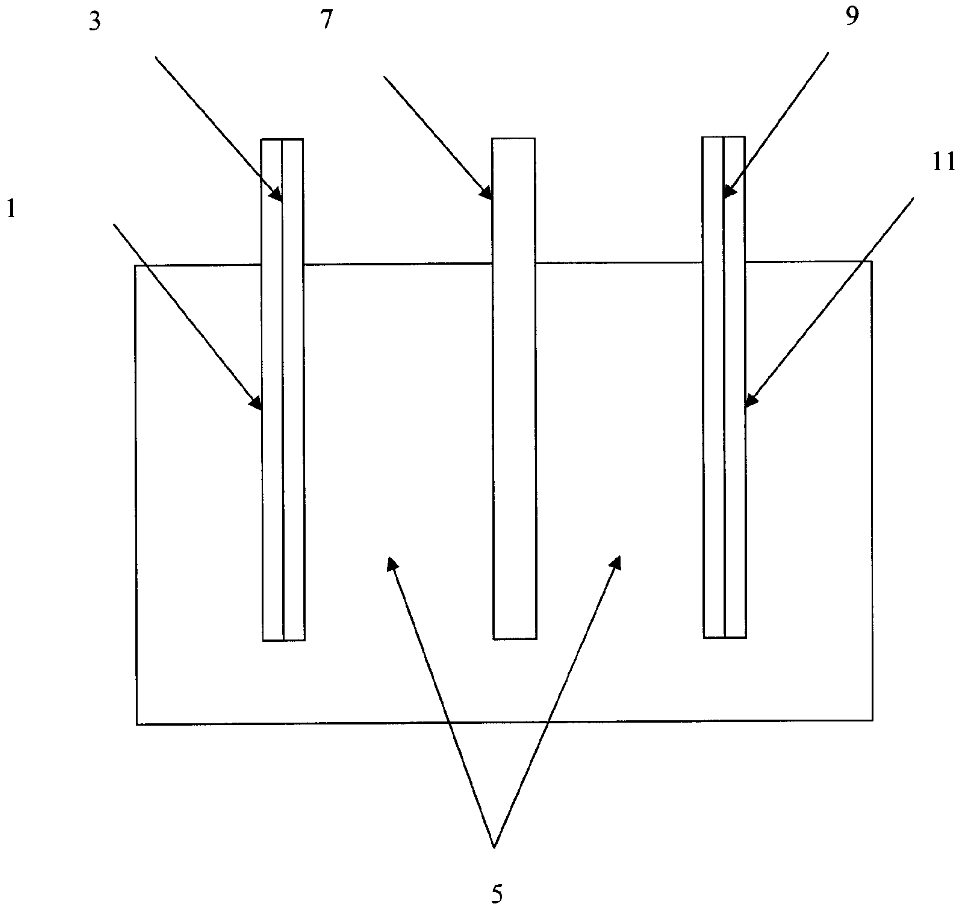


Figure 3

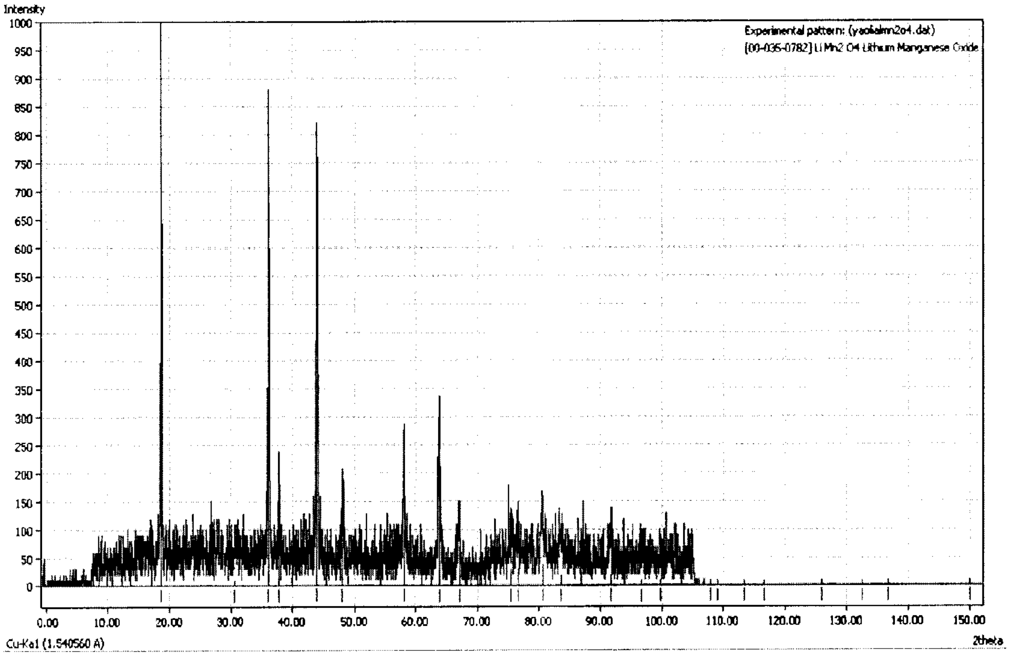

Intensity
1000
950
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
Experimental pattern: (yaolialmn2o4.dat)
[00-035-0782] Li Mn2 O4 Lithium Manganese Oxide
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
120.00
130.00
140.00
150.00
Cu-Ka1 (1.540560 A)
2theta

Figure 4

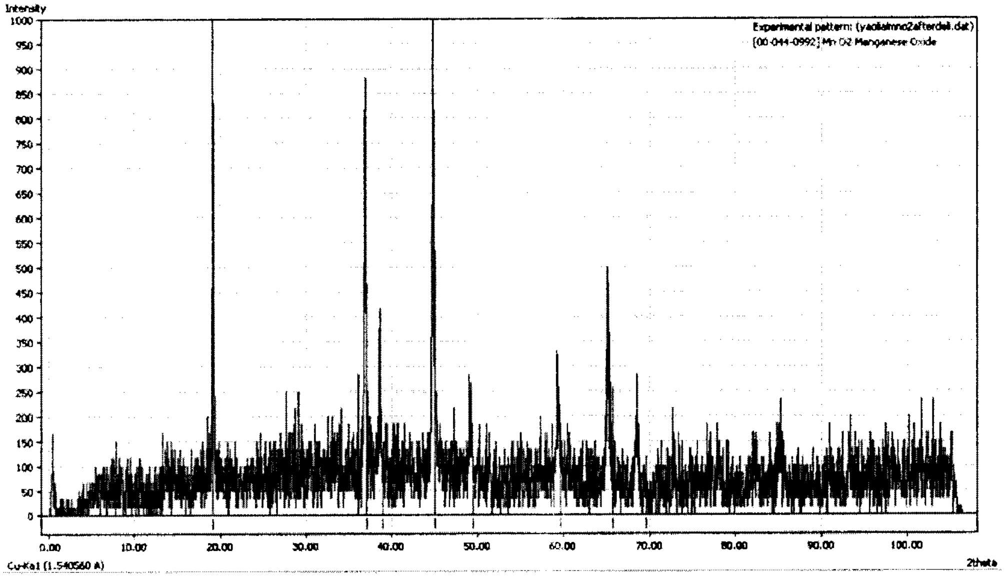
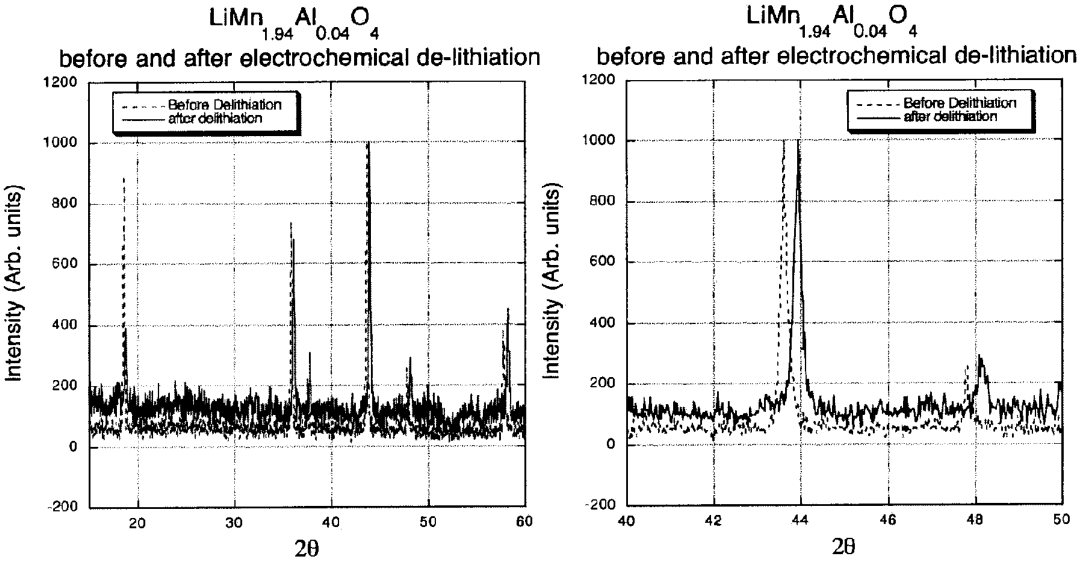

Intensity
1000
950
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
Experimental pattern: (yaoliahmno2afterdel.dat)
[00-044-0992] Mn O2 Manganese Oxide
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
Cu-Ka1 (1.540560 A)
2theta

Figure 5



$LiMn_{1.94}Al_{0.04}O_4$
before and after electrochemical de-lithiation
Before Delithiation
after delithiation
Intensity (Arb. units)
1200
1000
800
600
400
200
0
-200
20
30
40
50
60
2θ
$LiMn_{1.94}Al_{0.04}O_4$
before and after electrochemical de-lithiation
Before Delithiation
after delithiation
Intensity (Arb. units)
1200
1000
800
600
400
200
0
-200
40
42
44
46
48
50
2θ

A

B

Figure 6

De-Lithiated Al-Dopedλ-MnO2, Dense AC (0.56 g/cm^3)
Cycled in 1 M Na2SO4,
CV Analyses; 0.5 mV/Sec
(Data shown after 10 conditioning cycles in μelectrode Config)

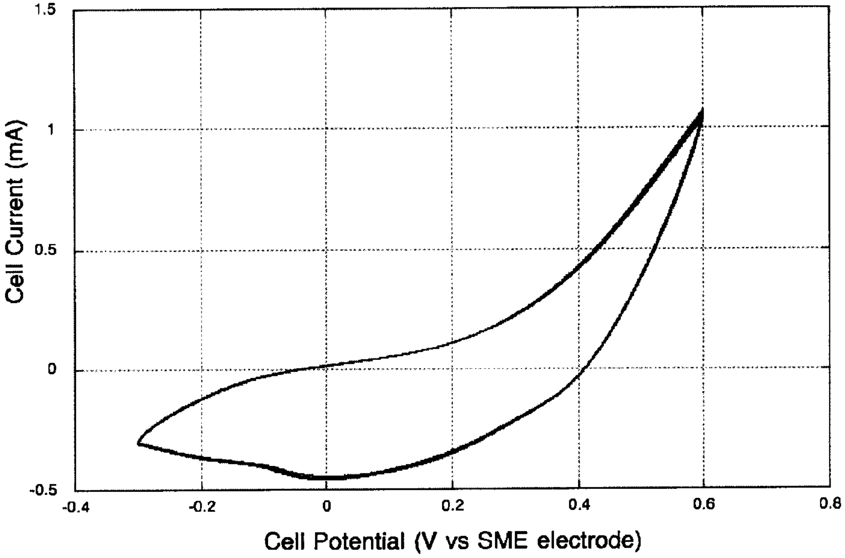


Figure 7

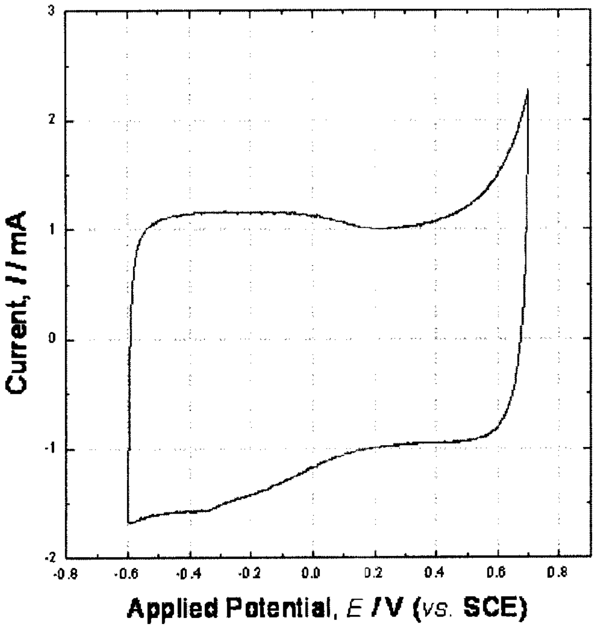

Current, I / mA
3
2
1
0
-1
-2
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
Applied Potential, E / V (vs. SCE)

Figure 8

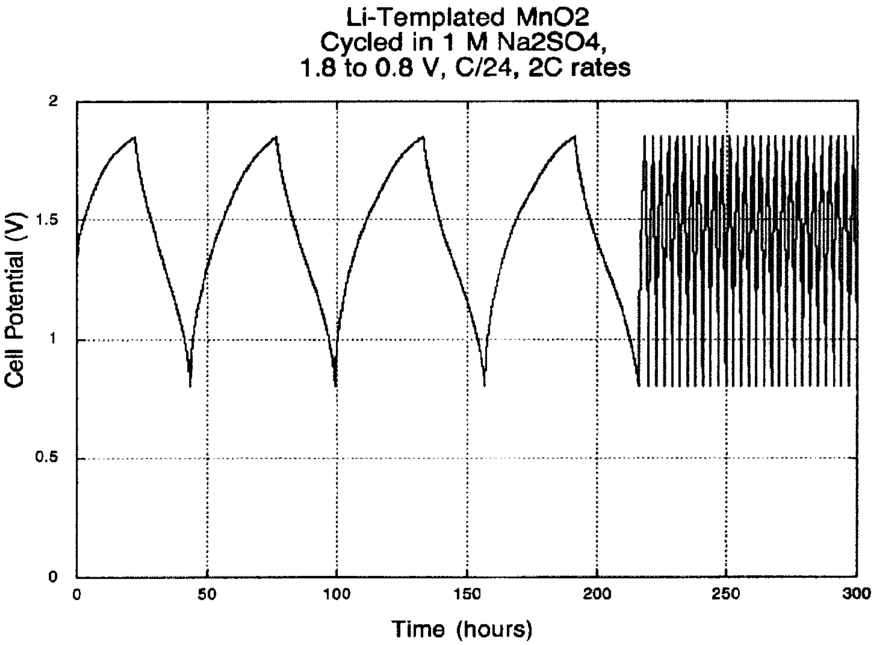
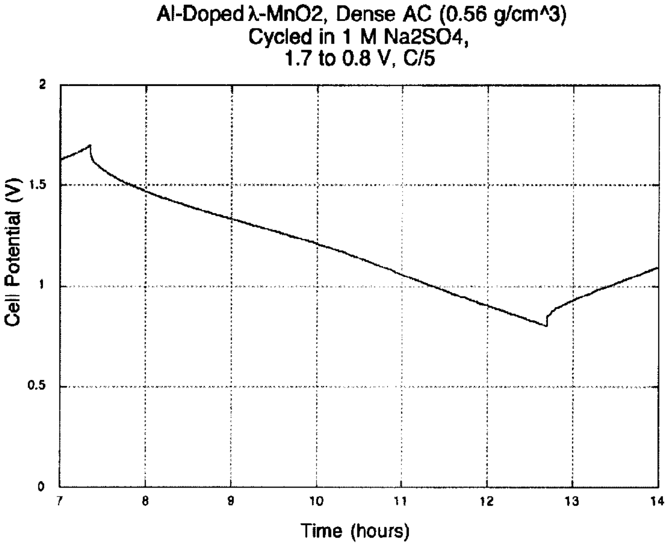

Li-Templated MnO2
Cycled in 1 M Na2SO4,
1.8 to 0.8 V, C/24, 2C rates
Cell Potential (V)
0
0.5
1
1.5
2
0
50
100
150
200
250
300
Time (hours)

Figure 9A



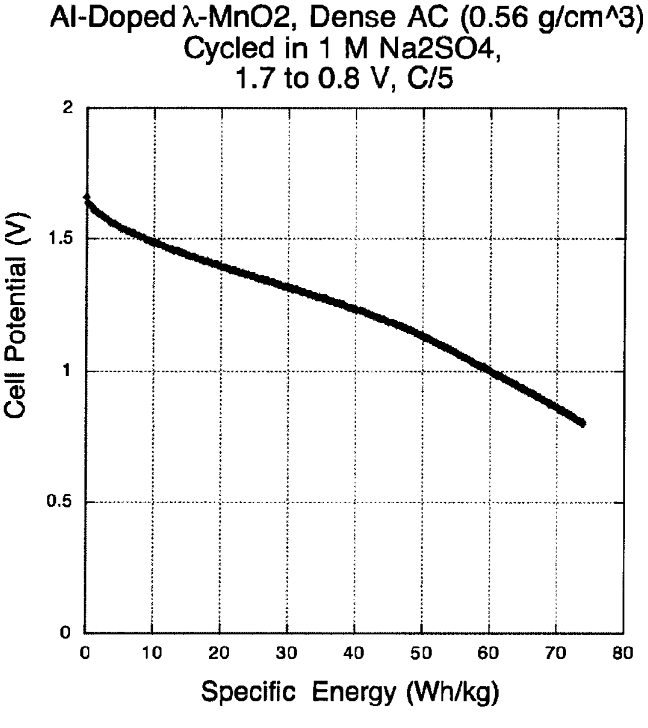


Figure 9B

Figure 10

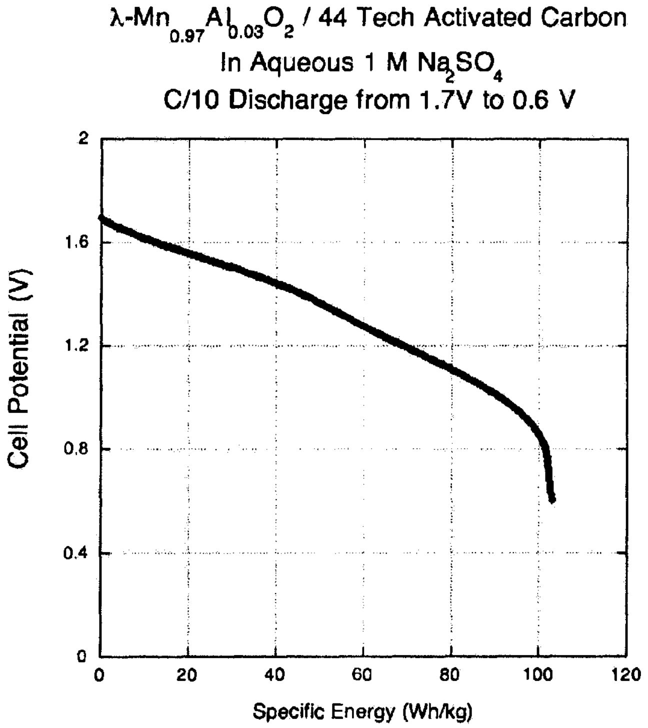
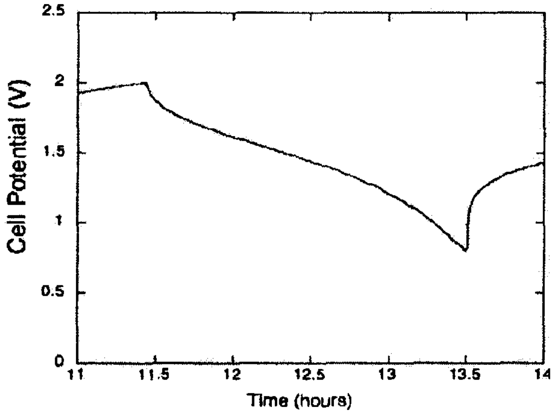

λ-$Mn_{0.97}Al_{0.03}O_2$ / 44 Tech Activated Carbon
In Aqueous 1 M Na_2SO_4
C/10 Discharge from 1.7V to 0.6 V
Cell Potential (V)
2
1.6
1.2
0.8
0.4
0
0
20
40
60
80
100
120
Specific Energy (Wh/kg)

Figure 11A


Cycling of Al-doped Spinel NaMn2O4 made via Electrochemical Li/Na ion exchange in Fresh Na2SO4 Aqueous electrolyte

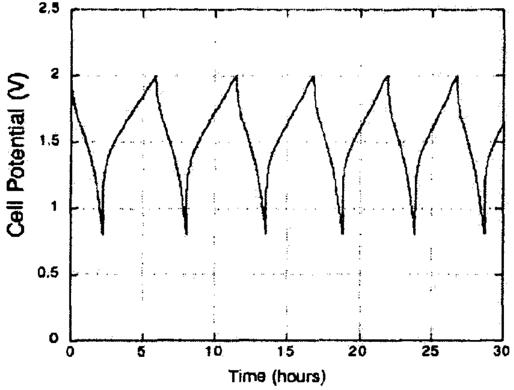

Cycling of Al-doped λ-MnO2 (fully de-lithiated Al-doped spinel LiMn2O4) in Fresh Na2SO4 Aqueous electrolyte
0.5 mA charge/discharge current
Cathode mass < 0.05 g

Figure 11B

Figure 12A

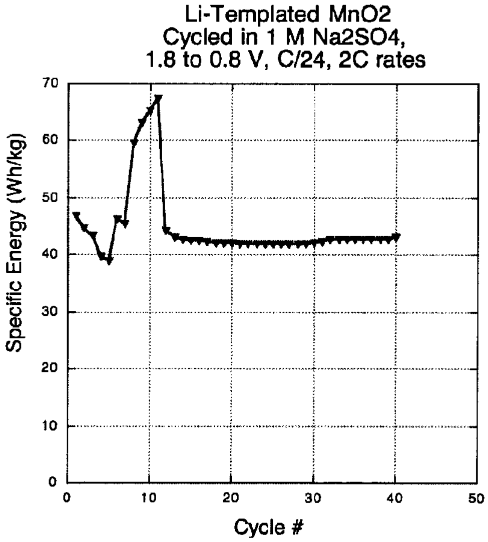
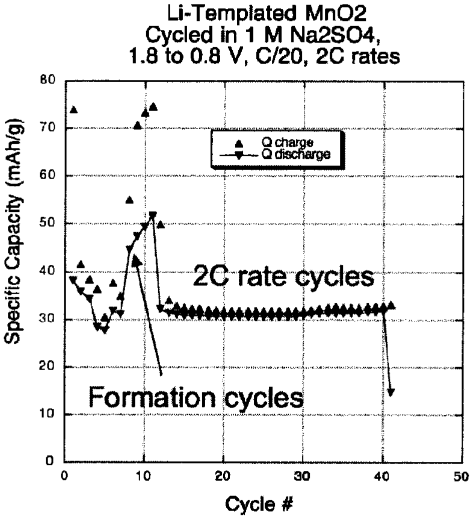


Figure 12B



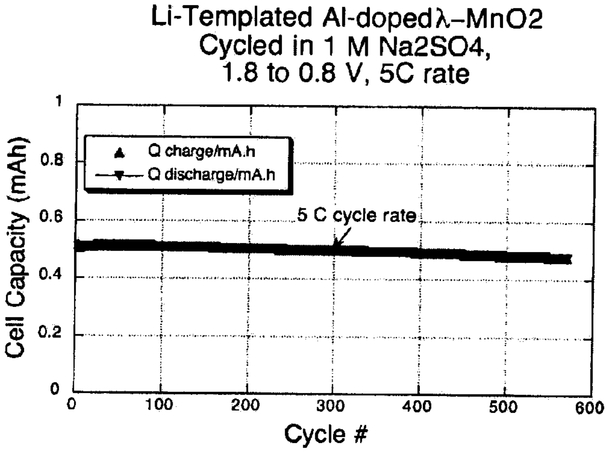


Figure 12C

Figure 13

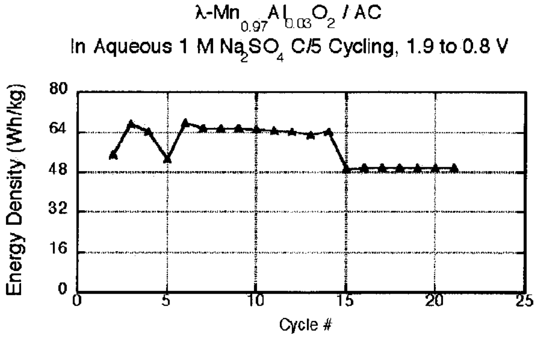

λ-Mn$_{0.97}$Al$_{0.03}$O$_2$ / AC
In Aqueous 1 M Na$_2$SO$_4$ C/5 Cycling, 1.9 to 0.8 V
Energy Density (Wh/kg)
80
64
48
32
16
0
0
5
10
15
20
25
Cycle #

Figure 14

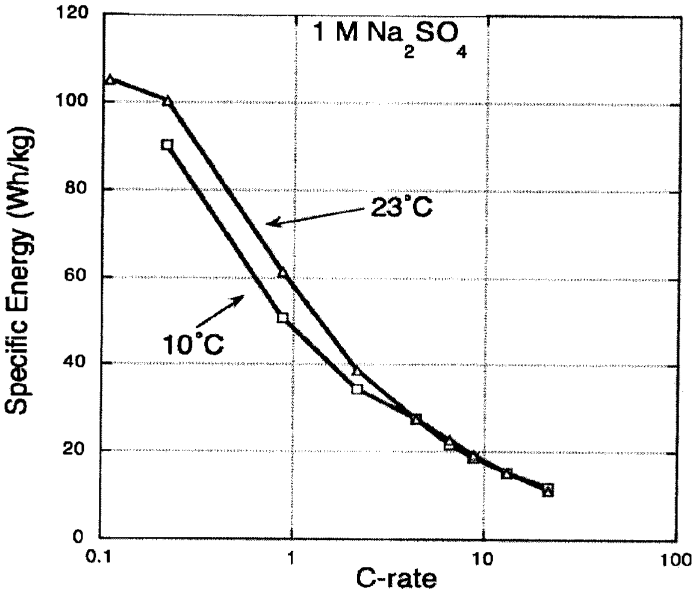

1 M Na_2SO_4
23°C
10°C
Specific Energy (Wh/kg)
C-rate
0
20
40
60
80
100
120
0.1
1
10
100

Figure 15

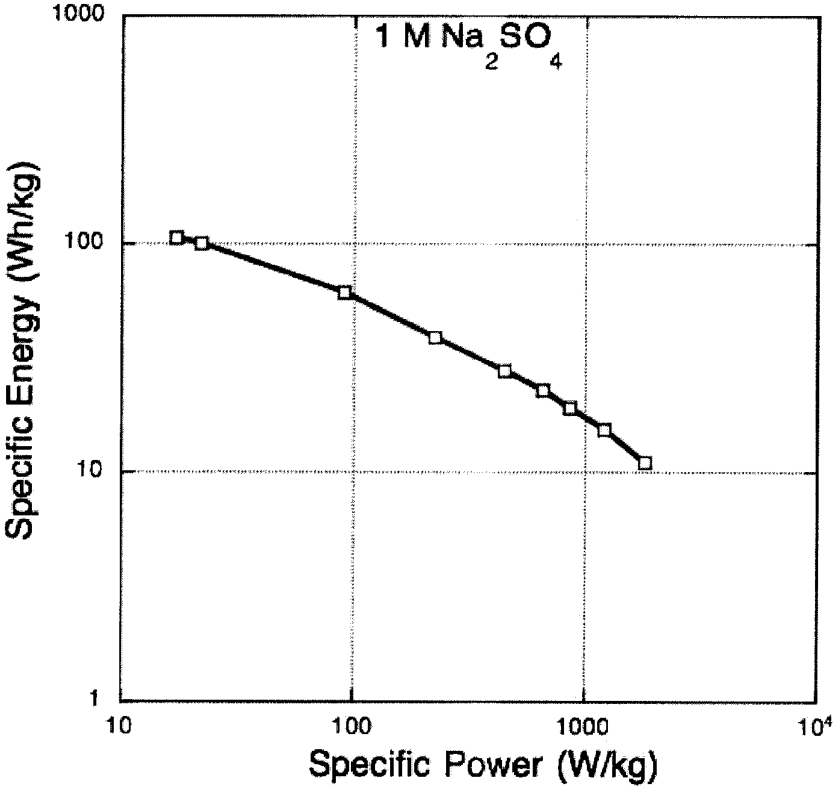

1 M Na_2SO_4
Specific Energy (Wh/kg)
1000
100
10
1
10
100
1000
10^4
Specific Power (W/kg)

Figure 16

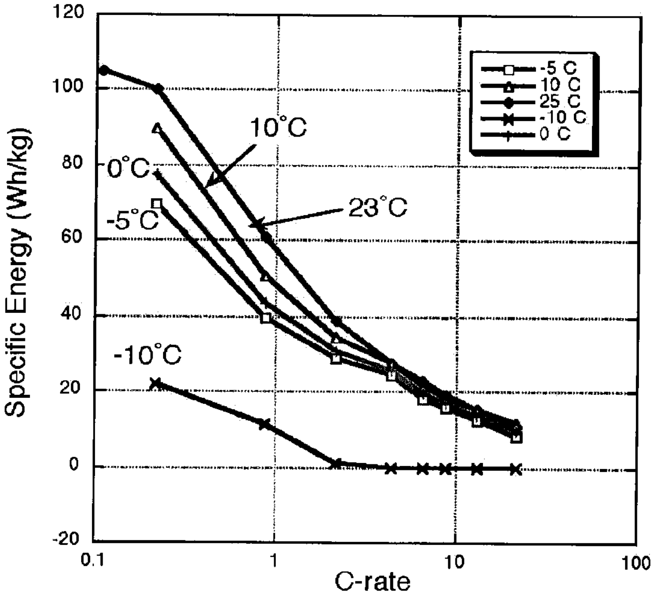

120
100
80
60
40
20
0
-20
Specific Energy (Wh/kg)
0.1
1
10
100
C-rate
-5 C
10 C
25 C
-10 C
0 C
10°C
23°C
0°C
-5°C
-10°C

Figure 17

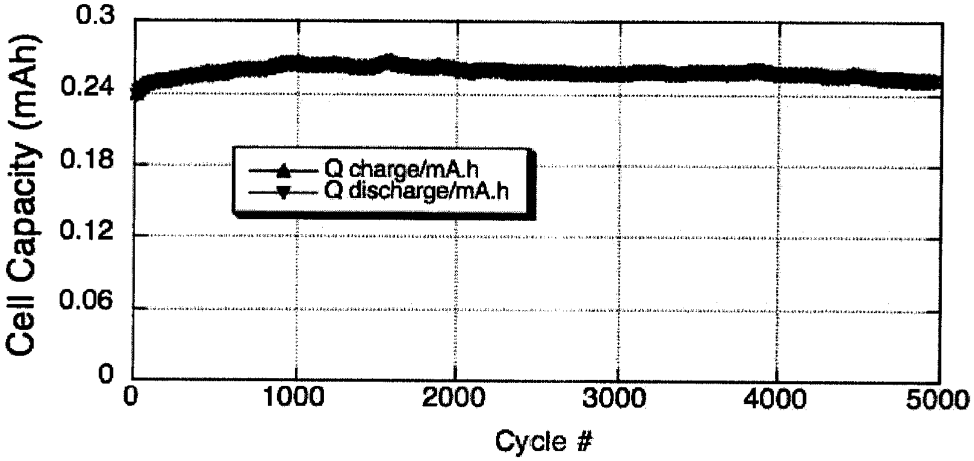

0.3
0.24
0.18
0.12
0.06
0
Cell Capacity (mAh)
0
1000
2000
3000
4000
5000
Cycle #
▲ Q charge/mA.h
▼ Q discharge/mA.h

Figure 18

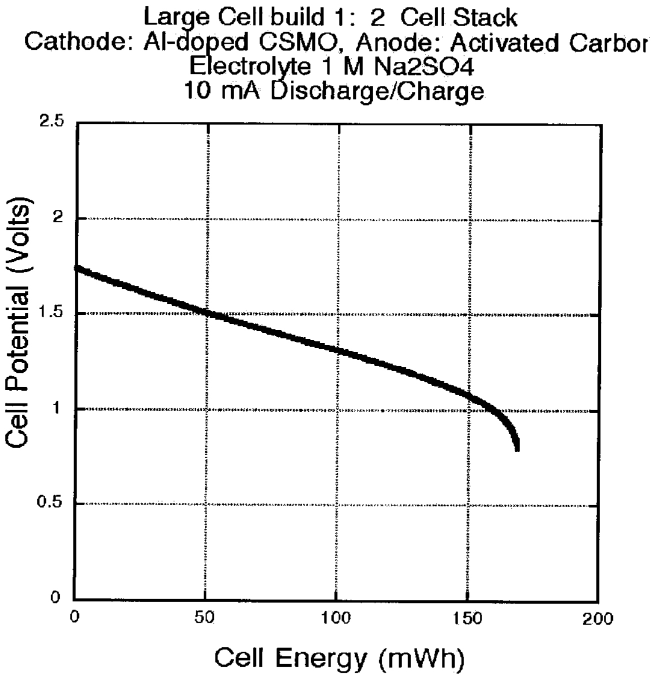

Large Cell build 1: 2 Cell Stack
Cathode: Al-doped CSMO, Anode: Activated Carbor
Electrolyte 1 M Na2SO4
10 mA Discharge/Charge
Cell Potential (Volts)
2.5
2
1.5
1
0.5
0
0
50
100
150
200
Cell Energy (mWh)

Figure 19

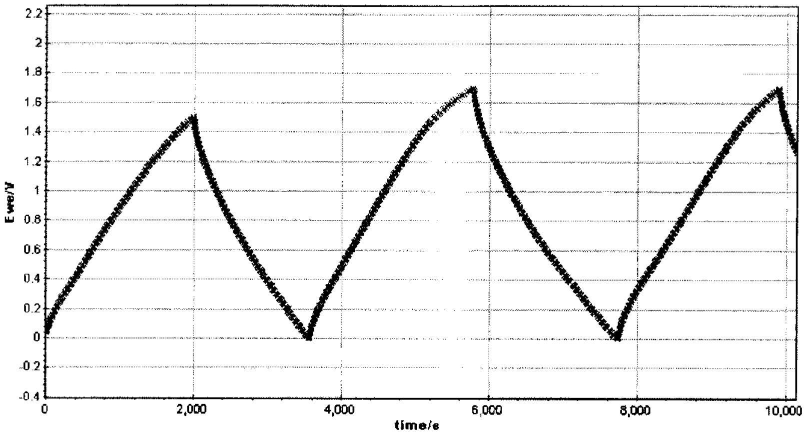

2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
E we/V
0
2,000
4,000
6,000
8,000
10,000
time/s

Figure 20A

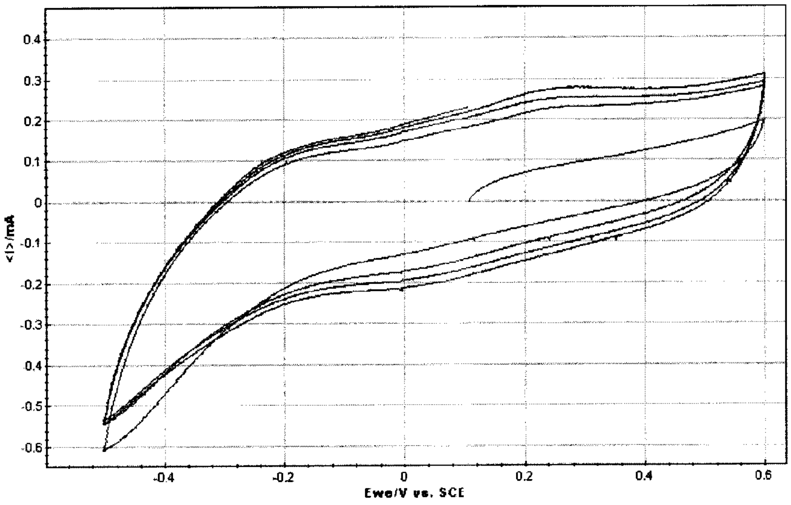


Figure 20B

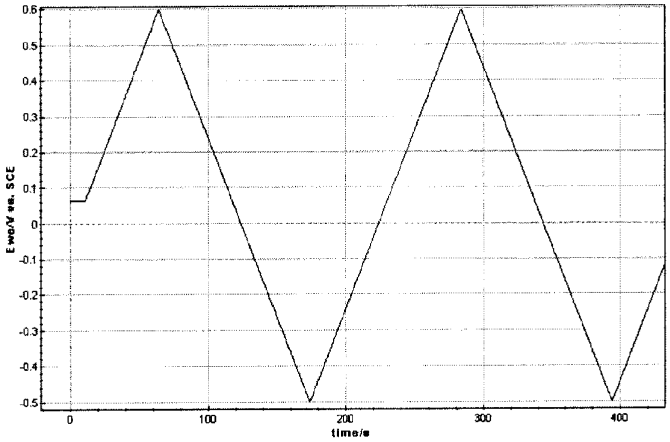


Figure 21

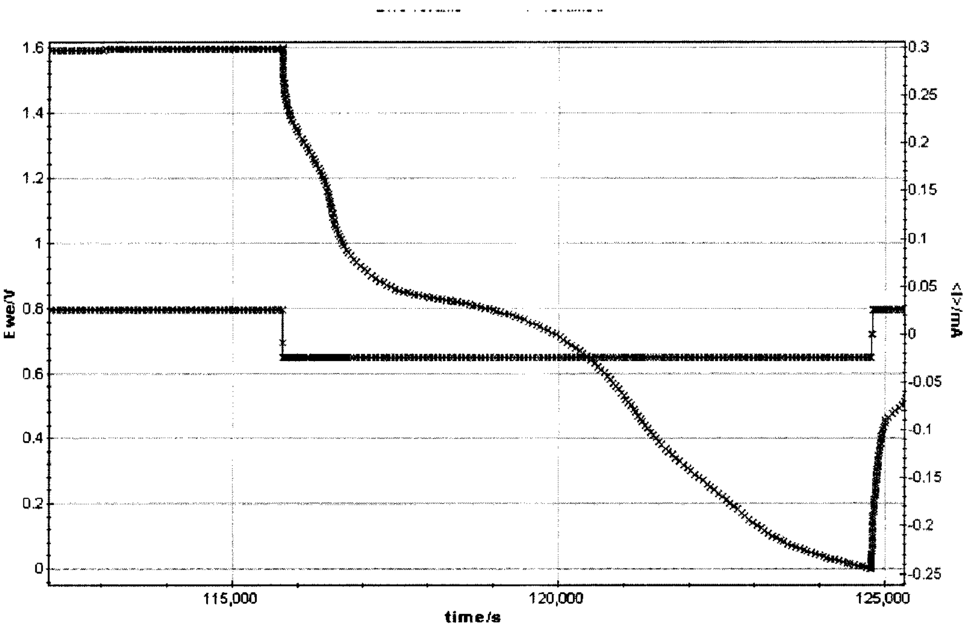

1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
E we/V
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
<I>/mA
115,000
120,000
125,000
time/s

Figure 22

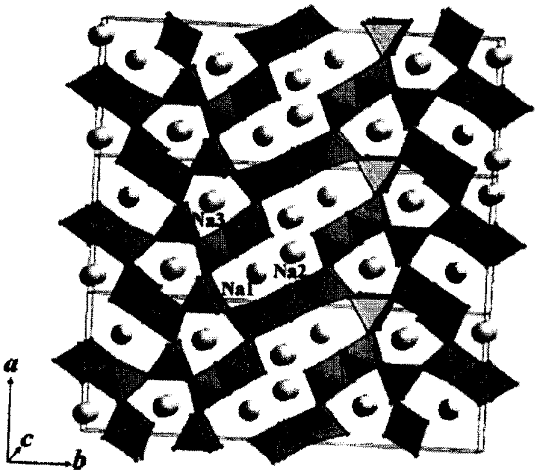


Figure 23

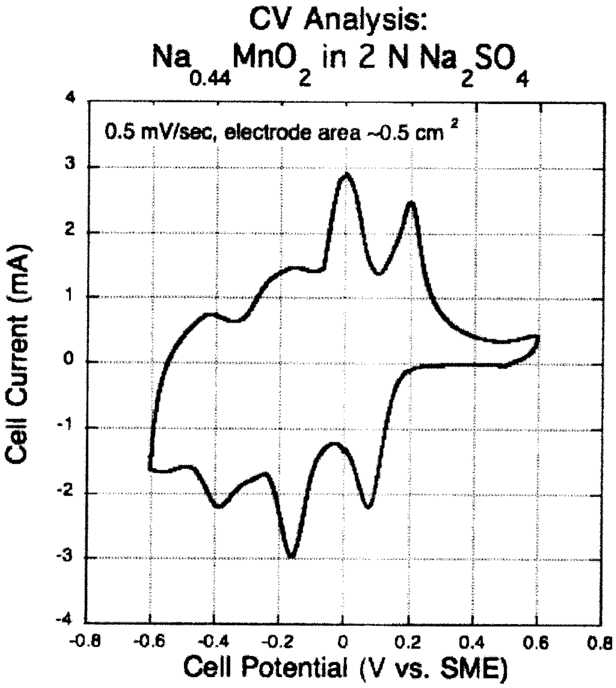

CV Analysis:
$Na_{0.44}MnO_2$ in 2 N Na_2SO_4
0.5 mV/sec, electrode area ~0.5 cm ^{2}
Cell Current (mA)
4
3
2
1
0
-1
-2
-3
-4
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
Cell Potential (V vs. SME)

Figure 24

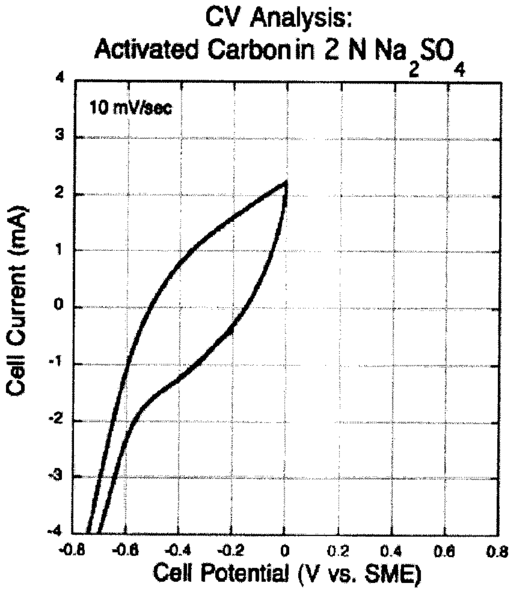

CV Analysis:
Activated Carbon in 2 N Na_2SO_4
10 mV/sec
Cell Current (mA)
4
3
2
1
0
-1
-2
-3
-4
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
Cell Potential (V vs. SME)

Figure 25

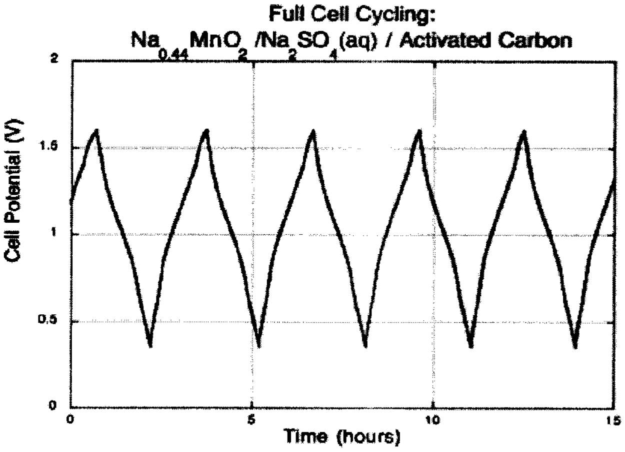

Full Cell Cycling:
$Na_{0.44}MnO_2$ /Na_2SO_4(aq) / Activated Carbon
Cell Potential (V)
2
1.5
1
0.5
0
0
5
10
15
Time (hours)

Figure 26

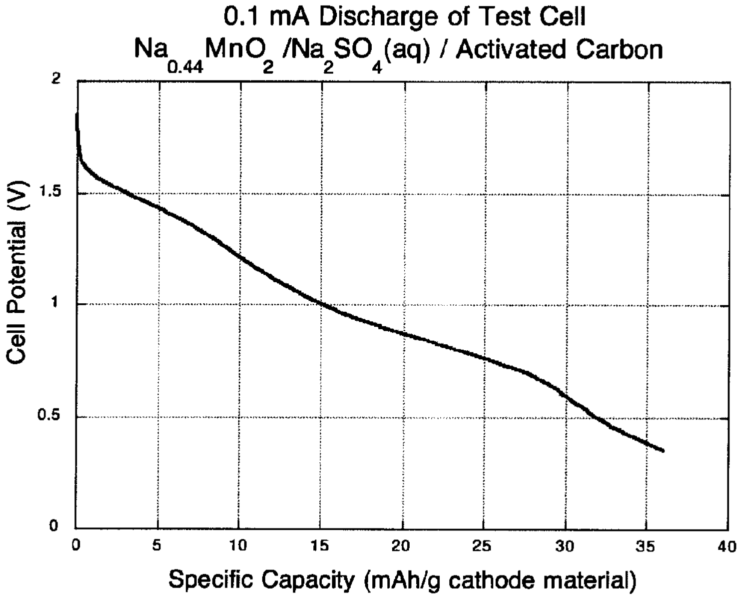

0.1 mA Discharge of Test Cell
$Na_{0.44}MnO_2$ /Na_2SO_4(aq) / Activated Carbon
Cell Potential (V)
2
1.5
1
0.5
0
0
5
10
15
20
25
30
35
40
Specific Capacity (mAh/g cathode material)

Figure 27

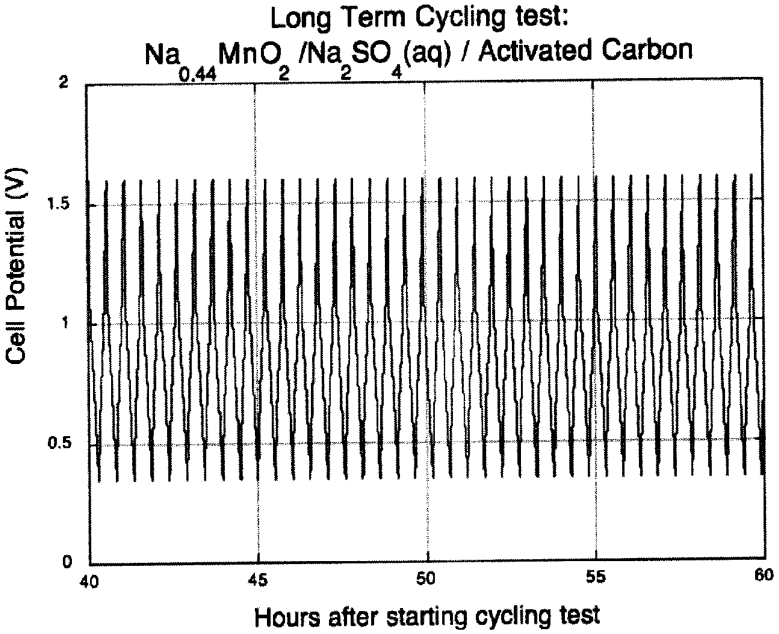

Long Term Cycling test:
$Na_{0.44}MnO_2$ /Na_2SO_4(aq) / Activated Carbon
Cell Potential (V)
0
0.5
1
1.5
2
40
45
50
55
60
Hours after starting cycling test

Figure 28

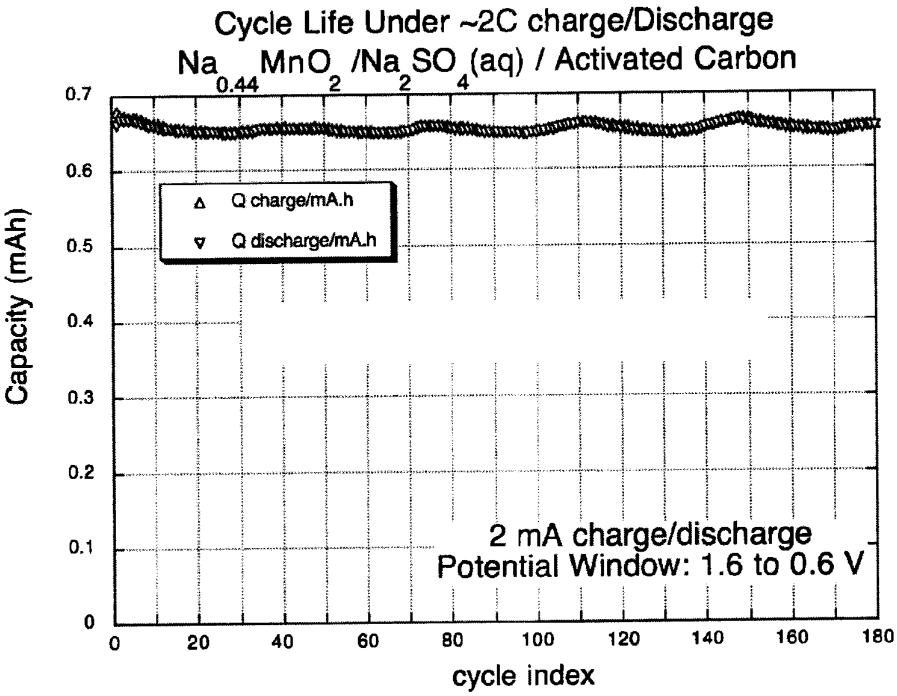

Cycle Life Under ~2C charge/Discharge
Na0.44MnO2 /Na2SO4(aq) / Activated Carbon
Capacity (mAh)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
100
120
140
160
180
cycle index
Δ Q charge/mA.h
∇ Q discharge/mA.h
2 mA charge/discharge
Potential Window: 1.6 to 0.6 V

Figure 29

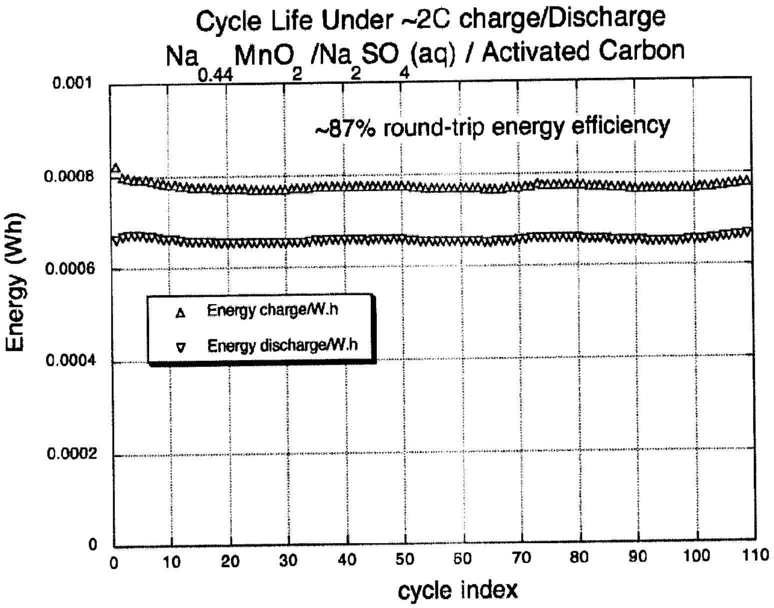
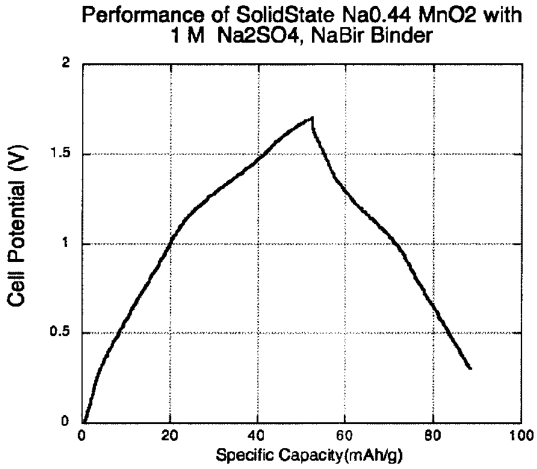

Cycle Life Under ~2C charge/Discharge
$Na_{0.44}MnO_2$ /Na_2SO_4(aq) / Activated Carbon
~87% round-trip energy efficiency
Energy (Wh)
0.001
0.0008
0.0006
0.0004
0.0002
0
cycle index
0
10
20
30
40
50
60
70
80
90
100
110
△ Energy charge/W.h
▽ Energy discharge/W.h

Figure 30A



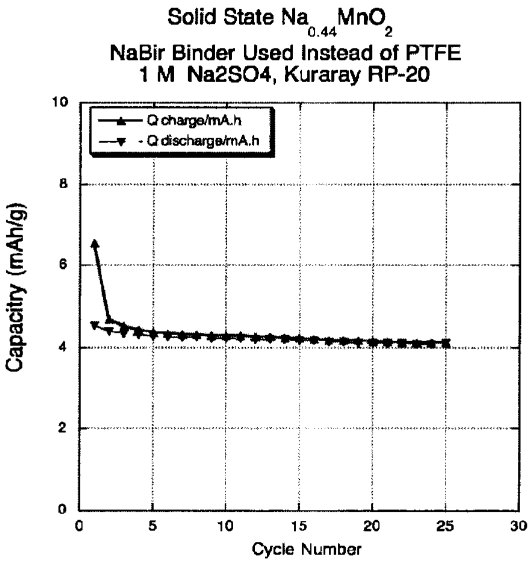


Figure 30B