The Importance of Solid Electrolyte Interphase Formation for Long Cycle Stability Full-Cell Na-Ion Batteries

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Abstract

Na-ion battery, as an alternative high-efficiency and low-cost energy storage device to Li-ion battery, has attracted wide interest for electrical grid and vehicle applications. However, demonstration of a full-cell battery with high energy and long cycle life remains a significant challenge. Here, we investigated the role of solid electrolyte interphase (SEI) formation on both cathodes and anodes and revealed a potential way to achieve long-term stability for Na-ion battery full-cells. Pre-cycling of cathodes and anodes leads to preformation of SEI, and hence mitigates the consumption of Na ions in full-cells. The example full-cell of Na_{0.44}MnO₂-hard carbon with pre-cycled and capacity-matched electrodes can deliver a specific capacity of ~116 mAh/g based on Na_{0.44}MnO₂ at 1C rate (1C = 120 mA/g). The corresponding specific energy is ~313 Wh/kg based on the cathode. Excellent cycling stability with ~77% capacity retention over 2000 cycles was demonstrated at 2C rate. Our work represents a leap forward in Na-ion battery development.

Keywords: Na-ion battery full cell, long cycle stability, solid electrolyte interphase

Introduction

With the growing use of electric vehicles and extensive implementation of intermittent renewable energy in electrical grids, the needs for low-cost and high-efficiency large-scale energy storage devices has risen significantly.^[1-2] Li-ion battery chemistry dominates the energy storage technologies for portable electronics because of the superior performance in power, energy density and cycle life. Yet it is costly, and its widespread application for transportation and large-scale stationary storage poses great concern regarding its limited and geographically constrained reserves. Because Na-ion has similar electrochemistry to Li-ion and sodium resources (e.g. NaCl, Na₂CO₃) are abundant in the Earth's crust, widely available, and inexpensive, Na-ion batteries are expected to be a high-efficiency and low-cost alternative to Li-ion batteries as energy storage devices.^[2-6]

In the last few years, extensive effort has been made on the development of aqueous and non-aqueous Na-ion batteries. Aqueous Na-ion batteries such as Na_{0.44}MnO₂-active carbon, Na_{0.44}MnO₂-NaTi₂(PO₄)₃ and Prussian blue materials with open framework have been demonstrated as high power systems with high cycling stability.^[7-13] Capacity retention of nearly 100% over thousands of cycles has been obtained with some systems.^[7-13] However, a main drawback of the aqueous system is the low capacity and energy density related to the narrow operating voltage window.

In order to fully exploit the capacity and energy density of Na-ion batteries, various kinds of cathode (Na_{0.44}MnO₂, NaCrO₂, NaCoO₂, NaFeO₂, NaVO₂, V₂O₅, Na_xFe_{1/2}Mn_{1/2}O₂, NaNi_{1/2}Mn_{1/2}O₂, Na_{2/3}Ni_{1/3}Mn_{2/3}O₂, Na(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂, Na(Ni_{1/3}Fe_{1/3}Mn_{1/3})O₂, Na₃V₂(PO₄)₃, Na₃V₂(PO₄)₂F₃, Prussian blue materials, etc.)^[3-6, 14-33] and anode materials (hard carbon, carboxylate-based organic material, Sn/Sb/Ni/Pb metal/metal alloy, phosphorus and phosphorus-based compounds, sodium titanates, and transitional metal oxides/sulfides, etc.)^[3-6, 34-49] have been developed and examined in non-aqueous electrolyte systems. For example, progress has been made on the development of various kinds of metal oxide and pyrophosphate cathodes,^[14-15] bio-derived hard carbon anode materials, and antimony (Sb)-based anodes.^[34-36,41] Hard carbon materials from waste bio-materials such as banana peels not only have improved capacity, cycling stability, and rate performance, but also are

low cost and environmentally benign.^[35] Sb-based alloy anodes can have high capacity (>400 mAh/g) and stable cycling up to hundreds of cycles with ultrafine nanoparticles of <20 nm.^[41] Recently, phosphorus-based high capacity anode materials and cathodes of high operating voltage (>3 V) and high capacity (>150 mAh/g) such as P2-Na_{2/3}[Fe_{1/2}Mn_{1/2}]O₂, Na₂Mn^{II}[Mn^{II}(CN)₆], and Na_{1.92}Fe[Fe(CN)₆] also have been developed.^[20,26-29,31,42-48] Na-ion batteries, with an electrode energy density competitive with Li-ion batteries, are on the way.

Electrolytes and electrolyte additives also have been investigated for optimum performance of the electrode materials. The correlation of battery performance with different combinations of solvents such as ethylene carbonate, propylene carbonate, and dimethyl carbonate has been investigated.^[50-52] Electrolyte additives such as fluorinated ethylene carbonate have been demonstrated to effectively improve the cycling stability of Sn-/Sb-/P-based alloy-type anodes or the first-cycle Coulombic efficiency of metal oxide cathodes.^[39-48]

Not only has much work been done on evaluating electrode materials in half-cells (using metallic Na as the counter electrode), but demonstration have also been attempted on full-cells (without using metallic Na) with metal oxides (Na[Ni_{1/2}Mn_{1/2}]O₂, Na[Fe_{1/3}Ni_{1/3}Mn_{1/3}]O₂, etc.), phosphate cathodes [Na₃V₂(PO₄)₃, Na₃V₂(PO₄)₂F₃ and Na₄Co₃(PO₄)₂P₂O₇, etc.] and organic materials.^[6,16,18,21,22,25,28,31-33,52] For example, Komaba et al. reported the Na[Ni_{1/2}Mn_{1/2}]O₂-hard carbon full-cell, which has an operating voltage of ~3 V and an estimated specific energy density of ~60% of the high-energy LiCoO₂-graphite system.^[52] The full-cell of the cathode with Sn-hard carbon delivers a specific capacity of ~120 mAh/g, but the retention decreases to ~60% within 50 cycles.^[52] The full-cell of Na[Fe_{1/3}Ni_{1/3}Mn_{1/3}]O₂-hard carbon also operates at an average voltage of ~3 V with ~120 mAh/g reversible capacity based on the positive electrode.^[18] It also shows much improved cycling stability, with ~80% capacity retention over 150 cycles.^[18] Recently, metal oxide cathode material with chemical composition that varied from the inner end (Na[Ni_{0.75}Co_{0.02}Mn_{0.23}]O₂) to the outer end (Na[Ni_{0.58}Co_{0.06}Mn_{0.36}]O₂) delivered a discharge capacity of 140 mAh/(g-oxide) and ~80% capacity retention over 300 cycles in a full-cell with a hard carbon anode.^[28]

For Na-ion battery to be more competitive among the technologies for electrical grids and vehicles, it is crucial to demonstrate Na-ion battery full-cells with high energy (>300 Wh/kg based on the cathode) and long cycle life (>1000 cycles). Yet it is very challenging, for several reasons. 1) Full-cells have no metallic Na but two Na insertion/alloy materials as cathodes and anodes. The Na ion usually stocks in the cathode material. Hence, full-cells, unlike half-cells with excess Na from the metal counter electrode, have limited Na in reserve. 2) Cathodes and anodes in full-cells need to perform maximally and also be balanced with each other. Hence, the full-cell performance, compared to that of a half-cell, is affected by many more factors, particularly the specific capacity and mass loading of cathodes and anodes, the charge-discharge voltage window and current density, and Coulombic efficiencies of both cathodes and anodes. 3) Some other issues related to cell geometry and assembly process along with the above complications make it very challenging to obtain full-cells with good performance.

Here, we demonstrated the feasibility of high-energy and long-cycle life Na-ion battery full-cells using $\text{Na}_{0.44}\text{MnO}_2$ -hard carbon as the model system. We synthesized $\text{Na}_{0.44}\text{MnO}_2$ through a simple solid-state reaction between Na_2CO_3 and MnO and achieved top half-cell performance against Na metal. A specific capacity of ~ 100 mAh/g with $\sim 79\%$ capacity retention over 2000 cycles was demonstrated between 2.0 and 3.7 V at 1C rate (1C = 120 mA/g). We exceeded good half-cell performance for commercial hard carbon over 500 cycles at different current densities from 50 to 500 mA/g. We also investigated the role of solid electrolyte interphase (SEI) formation on both cathode and anode materials and revealed that the preformation of SEI enables long cycling stability of full-cells. With pre-cycled and capacity-matched electrodes, the $\text{Na}_{0.44}\text{MnO}_2$ -hard carbon full-cell can deliver a specific capacity of ~ 116 mAh/g based on $\text{Na}_{0.44}\text{MnO}_2$ at 1C rate (1C = 120 mA/g). The corresponding specific energy is ~ 313 Wh/kg based on the cathode. It also exhibits excellent cycling stability with $\sim 77\%$ capacity retention over 2000 cycles at 2C rate.

Materials and methods

Material synthesis

$\text{Na}_{0.44}\text{MnO}_2$ was prepared through a simple solid-state reaction using low cost precursors of Na_2CO_3 and MnO . In a typical synthesis, appropriate amounts of Na_2CO_3 (1.026 g) and MnO (2.8376 g) were added to a ball milling container and milled for 3 h with a small amount of isopropanol. The mixture was then dried thoroughly, pressed into a pellet and heated at 800°C for 20 h. Hard carbon from Kureha Battery Materials Japan Co. Ltd. was used as received.

Characterization

X-ray diffraction (XRD) spectra were obtained on a Philips X'Pert X-ray diffractometer using a $\text{Cu K}\alpha$ sealed tube ($\lambda = 1.54178 \text{ \AA}$) at 0.5°/min. Selective area electron diffraction (SAED) patterns and high resolution transmission electron microscopy (HRTEM) images were collected from an FEI Titan 80-300 microscope with an image Cs corrector. Scanning TEM high angle annular dark field (STEM-HAADF) imaging was performed on an FEI Titan 80-300 microscope with a probe Cs corrector. The inner and outer collecting angles for STEM-HAADF images are 55 and 220 mrad, respectively. Both microscopes were operated at an accelerating voltage of 300 kV. Scanning electron microscopy (SEM) measurement was conducted on an FEI Helios Nanolab dual-beam focused ion beam SEM. X-ray photoelectron spectroscopy (XPS) was done on a Physical Electronics Instruments Quantum 2000 scanning X-ray microprobe. The cycled samples for TEM, SEM and XPS analysis were obtained from disassembled cells, washed three times with dimethyl carbonate, and vacuum-dried before characterization. The pre-cycled $\text{Na}_{0.44}\text{MnO}_2$ cathode was disassembled in the discharged state and the pre-cycled hard carbon anode in the charged state for SEM and XPS characterization. The full-cells with and without pre-cycled $\text{Na}_{0.44}\text{MnO}_2$ cathode and hard carbon anode were disassembled in the discharged state for characterization.

Electrochemical measurement

The $\text{Na}_{0.44}\text{MnO}_2$ cathode was prepared by mixing 80 wt% $\text{Na}_{0.44}\text{MnO}_2$, 10 wt% Super P, and 10 wt% polyvinylidene difluoride (PVDF) dissolved in N -methyl-2-pyrrolidone (NMP) to form a slurry, which was then pasted on an Al foil. The hard carbon anode was prepared by mixing 80 wt% commercial hard carbon (Kureha Battery Materials Japan Co. Ltd.), 10 wt% Super P, and 10 wt% PVDF dissolved in

NMP to form a slurry, which was then pasted on a Cu foil. After drying in vacuum at 70°C, the electrodes were punched and tested in coin cells. The electrode loading was about 2 mg/cm². The electrolyte was 1M NaClO₄ in a mixture of ethylene carbonate and dimethyl carbonate at a 1:2 weight ratio. A microporous membrane (Celgard 3501) was used as the separator. The coin cells were assembled in an argon-filled glove box. All the batteries were tested using galvanostatic charge-discharge protocols on an Arbin BT2000 battery testing system at room temperature. For half-cells, Na metal was used as the counter and the reference electrodes. Na_{0.44}MnO₂ cathodes were tested within a voltage range from 2.0 to 3.7 V or 2.0 to 4.0 V. Hard carbon anodes were cycled within a voltage range from 0.02 to 1.5 V. For full-cells, Na_{0.44}MnO₂ cathodes and hard carbon anodes were pre-cycled in half-cells for 3 cycles and then reassembled into full-cells. The pre-cycled Na_{0.44}MnO₂ cathodes were disassembled in the discharged state and the pre-cycled hard carbon anodes in the charged state for full-cell assembly. The cathode was limiting and the cathode-to-anode specific capacity loading ratio was 1:1.1 at 2C rate (1C = 120 mA/g). Full-cells were cycled within a voltage range from 1.5 to 4.1 V, 1.5 to 3.8 V, or 1.5 to 4.5 V. The current density for full-cell tests was calculated based on the weight of Na_{0.44}MnO₂. All of the specific weight-capacity and specific energy values in this paper were calculated based on the weight of Na_{0.44}MnO₂.

Results and discussions

As both cathodes and anodes need to perform maximally and also be balanced for full-cell assembly, we investigated the electrochemical performance and structural stability of Na_{0.44}MnO₂ cathodes and hard carbon anodes in half-cell design before moving on to study the full-cell performance.

Electrochemical performance and structural stability of Na_{0.44}MnO₂ in half-cells

Na_{0.44}MnO₂, also written Na₄Mn₉O₁₈, is known to be a very stable cathode material for Na-ion batteries.^[8,16,53-54] The Na_{0.44}MnO₂ obtained in this work showed top performance of the material in terms of capacity, cycling stability and rate performance in half-cell tests.

Figure 1a shows the typical cycling performance of a Na_{0.44}MnO₂ electrode between 2.0 and 3.7 V against Na metal. The half-cell was cycled at 0.1C (1C = 120 mA/g) for 3 formation cycles and then

tested at 1C rate for 2000 cycles. The specific discharge capacity of $\text{Na}_{0.44}\text{MnO}_2$ was ~ 109 mAh/g at 0.1C rate and ~ 100 mAh/g at 1C rate. The capacity retention was $\sim 79\%$ over 2000 cycles. The Coulombic efficiency for the first cycle (0.1C rate) was $\sim 82\%$. It quickly increased to $\sim 99.5\%$ in a couple of cycles and remained stable in the following 2000 cycles. Figure S1a shows the charge-discharge curves of the same $\text{Na}_{0.44}\text{MnO}_2$ electrode in Figure 1a at the 1st, 200th, 1000th, and 2000th cycles. All the charge-discharge curves, regardless of the formation cycles at 0.1C rate or the following 2000 cycles at 1C rate, have the representative plateaus, corresponding to the phase structure transitions. They are in good agreement with those of single crystalline nanowires and other literature results.^[8,16,53-54] The fact that the plateaus in the charge-discharge curves do not change over long-term cycling is consistent with the excellent structural stability that we will discuss later. This, together with the high Coulombic efficiency, ensures good redox reversibility and full-cell battery stability from the cathode side.

It must be noted that the discharge capacity of the $\text{Na}_{0.44}\text{MnO}_2$ sample is ~ 19 mAh/g lower while the first-cycle Coulombic efficiency is $\sim 30\%$ higher compared to our previous $\text{Na}_{0.44}\text{MnO}_2$ single crystalline nanowires.^[16] A main reason for the difference probably is that the cut-off voltage for charge is 3.7 V for the current work while it is 4 V for the nanowires.^[16] The difference in particle size and morphology also affects the electrochemical performance, and the effect will be discussed later. Good rate performance of the cathode is a prerequisite for a high power full-cell device. Figure 1b shows the representative rate performance of another $\text{Na}_{0.44}\text{MnO}_2$ electrode between 2.0 and 3.7 V. It delivers reversible capacities of ~ 107 mAh/g at 0.1C (12 mA/g), ~ 98 mAh/g at 1C (120 mA/g), 93 mAh/g at 2C (240 mA/g) and 84 mAh/g at 4C (480 mA/g). The excellent long-term cycling stability and rate performance of $\text{Na}_{0.44}\text{MnO}_2$ are important for the best full-cell performance.

The synthesized $\text{Na}_{0.44}\text{MnO}_2$ has highly crystalized orthorhombic structure as indicated by the strong diffraction peaks in the X-ray diffraction (XRD) pattern (Figure S2a). A low magnification transmission electron microscopy (TEM) image (Figure S2) shows that the $\text{Na}_{0.44}\text{MnO}_2$ has rod- or belt-/flake-like morphology with a size of several hundred nanometers. There are also large particle agglomerates

that do not show up in the TEM image. The particle size is larger than the nanowires obtained with the polymer-pyrolysis method,^[16] leading to a smaller surface area and better first cycle Coulombic efficiency (~75%) even in a wide voltage window of 2 to 4 V (Figure S3).

The change in fine structure between pristine and cycled (1000 cycles) $\text{Na}_{0.44}\text{MnO}_2$ was investigated carefully by high resolution TEM (HRTEM), scanning TEM high angle annular dark field (STEM-HAADF) and selected area electron diffraction (SAED). Figures 1c and 1d are HRTEM and STEM-HAADF images of a pristine $\text{Na}_{0.44}\text{MnO}_2$ particle, while Figures 1e and 1f are the HRTEM and STEM-HAADF images of a $\text{Na}_{0.44}\text{MnO}_2$ particle after it was cycled 1000 times between 2.0 and 3.7 V at 1C rate (1C = 120 mA/g). All the images were taken along the a-c plane, perpendicular to the [010] direction and match well with the atomic structure of $\text{Na}_{0.44}\text{MnO}_2$ in Figure 1g. Comparing these two sets of images and the atomic structure model, it can be concluded that the $\text{Na}_{0.44}\text{MnO}_2$ obtained has very stable lattice structure and undergoes little change even after 1000 cycles. SAED patterns also were taken to further confirm the structure stability. The $\text{Na}_{0.44}\text{MnO}_2$ before and after cycling has very similar single crystalline patterns (insets of Figures 1c and 1e). The superb structural stability before and after cycling further corroborates the excellent half-cell performance in Figure 1a and ensures it as an excellent cathode for subsequent full-cell assembly.

Structure and half-cell electrochemical performance of hard carbon

A structurally stable and high performance anode is as crucial as the cathode for the subsequent full-cell demonstration. Hard carbon is a low cost anode material of high capacity, low working voltage, and good cycling stability, all attributes supporting a Na-ion battery with high energy, long cycle life, and low cost.

Commercial hard carbon was characterized and excelled as high performance anodes. The XRD result shows no graphitic phase but a pronounced (002) peak indicating few-layer graphene sheets stacked in a highly disordered manner (Figure 2a). TEM and HRTEM characterization corroborate the XRD result. Particles of hard carbon have irregular apparent morphology at low magnifications (Figure 2b) and randomly stacked, disordered graphene layers under HRTEM (Figure 2c). It must be noted that

the commercial hard carbon is mainly micron-sized particles with low surface area and high tap density (contact the vendor for detailed information). It is just that TEM images have to be taken on small particles.

The hard carbon shows good half-cell performance in terms of capacity and cycling stability. Figure 2d shows the charge-discharge curves of a typical hard carbon half-cell cycled at different rates/current densities of 0.2C (50 mA/g), 0.5C (125 mA/g), 1C (250 mA/g) and 2C (500 mA/g). The stable specific discharge capacity delivered at each current density is ~218, ~155, ~102, and ~72 mAh/g, respectively. A two-stage discharge curve with features of a sloping curve from 1.5 to 0.1 V and a clear and long plateau around 0.1 V was obtained, in good agreement with the literature results.^[34-36, 52] Further analysis shows that the capacity ratio between the two parts of the discharge capacity is ~1:1 at a low rate/charge-discharge current density of 0.2C (50 mA/g). At high charge-discharge current densities, both parts of the discharge capacity decrease greatly. However, the plateau around 0.1 V shortened more abruptly with the capacity below 0.1 V decreased from 111 mAh/g (0.2C, 50 mA/g current density), to 70 mAh/g (0.5C, 125 mA/g), 31 mAh/g (1C, 250 mA/g), and 14 mAh/g (2C, 500 mA/g). This indicates that the Na-ion intercalation into hard carbon only has mediocre rate performance if the voltage range is from 0 to 0.1 V while a good rate will be obtained if it is mostly between 0.1 and 1.5 V.

Figure 2e shows the cycling performance of the specific capacity and Coulombic efficiency of the same hard carbon electrode in Figure 2d. Hard carbon shows good long-term cycling stability. The specific capacity recovered to ~214 mAh/g when the current density was switched back to 0.2C (50 mA/g) after 400 cycles at different rates/current densities of 0.2C (50 mA/g), 0.5C (125 mA/g), 1C (250 mA/g) and 2C (500 mA/g). The capacity retention was 92% after another 100 cycles at 0.2C (50 mA/g). The Coulombic efficiency, however, was poor. It started at ~70% for the first-cycle and increased to ~99% after a few cycles. Because of the mixed electrochemical performance of hard carbon, which has high capacity and good cycling stability but poor Coulombic efficiency and poor

rate performance, special attention is needed in terms of electrode balancing with a $\text{Na}_{0.44}\text{MnO}_4$ cathode for full-cell assembly.

We tried to characterize the hard carbon structure after long-term cycling. However, it was very difficult because the hard carbon was coated with a thick layer of SEI, which was from electrolyte decomposition over the hundreds of cycles. From the electrochemical test, we believe it is safe to say that a hard carbon anode should have stable structure for at least hundreds of cycles.

Investigation of SEI formation in the pre-cycle treatment

Excellent full-cell performance has been demonstrated in several aqueous Na-ion battery systems.^[7-13] However, demonstration of a non-aqueous Na-ion battery full-cell with long cycle life and high energy is very challenging, even though highly stable cathode and anode materials such as $\text{Na}_{0.44}\text{MnO}_2$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ have been demonstrated in half-cells.^[16,55-56] It is believed that the major obstacle is related to the low Coulombic efficiency that originates from the non-aqueous electrolyte and the wide voltage window.

Ideally, if both cathodes and anodes have 100% Coulombic efficiency (full reversibility and no side reactions at cathodes or anodes), good full-cell performance will be obtained after matching the capacity of the electrodes. Yet in practice, cathodes and anodes usually have a first-cycle Coulombic efficiency much lower than 100%. The non-aqueous electrolyte system has the advantages of large voltage window and high capacity, yet at the same time it presents problems/challenges. The solvents and salts in the non-aqueous electrolytes become oxidized at cathode surfaces at high charge voltage and reduced at anode surfaces at low discharge voltage, leading to the formation of SEI, low Coulombic efficiency in the first few cycles, large first-cycle irreversible capacity loss, and capacity fade in following cycles. A natural thought to address the challenge is to preform SEI layers on both cathode and anode before the full-cell assembly so that the side reactions and Na-ion consumption in subsequent full-cell cycling will be mitigated. It is known that an SEI layer forms on electrode surfaces when cycling the electrode in a half-cell against Na metal. The key is whether the

SEI layer preformed in pre-cycle of a half-cell can help to improve the full-cell performance and whether the full-cell could be assembled without much damage to the preformed SEI.

We developed a simple technique to minimize surface damage of pre-cycled electrodes by assembling the half-cell in a reverse order to that of conventional half-cells and transferring the electrode together with the spacer and separator for full-cell assembly (Figure S4). As shown in Figure S4a, the working electrode has intimate contact with the bottom can of a coin cell and has a separator on top. It is difficult to keep the pre-cycled working electrode intact when we collect it from the disassembled half-cell. However, the working electrode is in the middle of the cell using the reverse design (Figure S4b). We can almost keep the pre-cycled electrode surface untouched when we transfer it together with the spacer and separator.

Na_{0.44}MnO₂-hard carbon full-cells with cathodes and anodes of the same capacity ratio but different pre-cycle treatments were assembled (see detail in Experimental Section) and investigated for their full-cell performance and correlation to different SEI formation. Figure 3a shows the cycling stability and Coulombic efficiency of a full-cell assembled using electrodes that had no pre-cycle treatment. An initial capacity of ~27 mAh/g was obtained, and it faded quickly to <10 mAh/g. The Coulombic efficiency was <10% for the first cycle and ~90% after 100 cycles. According to the above half-cell data, Na_{0.44}MnO₂ has a low first-cycle efficiency of ~80%. The first-cycle Coulombic efficiency of hard carbon in half-cells is even lower, ~70%. Furthermore, it takes 2 to 3 more cycles for the Coulombic efficiency of Na_{0.44}MnO₂ and hard carbon to be >95% (Figures 1 and 2). Hence, it is believed that the low Coulombic efficiency of the cathode and the anode drained the limited Na ion stock in the Na_{0.44}MnO₂ cathode very quickly, resulting in low capacity, quick capacity fade, and poor Coulombic efficiency.

To further elucidate the importance of the SEI on full-cell performance, experiments were carried out to study Na_{0.44}MnO₂-hard carbon full-cells with only the cathode or the anode is pre-cycled. Figure 3b shows the cycling performance of a full-cell with a pre-cycled hard carbon anode. A capacity of ~75 mAh/g with capacity retention of ~70% at 0.5C rate (60 mA/g) was obtained. Figure 3c shows that a

full-cell with pre-cycled $\text{Na}_{0.44}\text{MnO}_2$ cathode has a capacity of ~ 88 mAh/g and capacity retention of $\sim 83\%$ at 0.5C rate (60 mA/g). The best full-cell performance was obtained by pre-cycling both cathode and anode (vide infra).

From the dramatic performance difference of full-cells with different pre-cycling treatments (Figure 3), it can be concluded that pre-cycling cathodes and anodes helps to improve the full-cell performance. To corroborate the conclusion that the good full-cell performance is because an SEI layer preformed in the pre-cycle treatment and remained stable in the following full-cell cycling, systematic characterization such as scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were employed to study the surface morphology and composition of the cathodes and anodes with and without pre-cycling treatment (Figures 4 and S5).

SEM images in Figures 4a and 4b show that the pre-cycled hard carbon anode (Figure 4a) and the control hard carbon anode cycled in a full-cell without pre-cycling treatment (Figure 4b) have amorphous coating on the surface indicating the formation of SEI on both hard carbon anodes. The corresponding XPS C1s spectra in Figure 4c corroborates the SEI formation. In Figure 4c (black curve), the pristine hard carbon anode shows typical features of carbon electrodes, with the most intense peak at ~ 284.5 eV, a shoulder peak around 286.7 eV, and a small peak at ~ 291 eV. After pre-cycling treatment (Figure 4c, red curve), the carbon signal at ~ 284.5 eV is significantly reduced and the pronounced peak is at ~ 289 eV with a shoulder at ~ 292 eV, in good agreement with the surface morphology (Figures 4a and S5): the hard carbon anode after pre-cycling treatment was covered with a thick SEI layer. The C1s spectrum of the anode cycled in a full-cell without pre-cycling treatment also shows greatly reduced signal at ~ 284 eV and formation of new peaks at higher binding energies, implying the formation of an SEI layer (Figure 4c, pink curve). However, the SEI composition is different from that of the hard carbon anodes with pre-cycling treatment. The pronounced C1s peak is at ~ 287 eV with a shoulder peak at ~ 286.7 eV and a small peak at ~ 292 eV. The different SEI composition is ascribed to different electrolyte decomposition: the SEI formed on pre-cycled hard carbon is in a half-cell vs. Na metal and has unlimited Na ion stock, while the SEI formed on hard

carbon in a full-cell without pre-cycling treatment has very limited Na ion stock and is formed vs. a $\text{Na}_{0.44}\text{MnO}_2$ cathode.

SEM images in Figures 4d and 4e show that the pre-cycled $\text{Na}_{0.44}\text{MnO}_2$ cathode (Figure 4d) has a layer of amorphous surface coating while the control $\text{Na}_{0.44}\text{MnO}_2$ cathode cycled in a full-cell without pre-cycling treatment (Figure 4e) is very similar to the pristine sample (Figure S5). The corresponding XPS Mn2p spectra of the pre-cycled $\text{Na}_{0.44}\text{MnO}_2$ cathode has almost no Mn2p signal (Figure 4f, red curve), indicating that a thick SEI layer was formed on the cathode surface during pre-cycling. The XPS Mn2p spectra of the control $\text{Na}_{0.44}\text{MnO}_2$ electrode cycled in a full-cell without pre-cycling treatment, however, shows two pronounced peaks at ~642 and 654 eV (Figure 4f, pink curve), similar to pristine $\text{Na}_{0.44}\text{MnO}_2$ electrode (Figure 4f, black curve). It indicates that the SEI layer on the $\text{Na}_{0.44}\text{MnO}_2$ electrode cycled in a full-cell without pre-cycling treatment is either very thin or does not have a good coverage. The result is in perfect match with the SEM observation of the electrode surface morphology difference in Figures 4d and 4e. It hence concluded that a good SEI layer was formed on the pre-cycled $\text{Na}_{0.44}\text{MnO}_2$ cathode while no or poor SEI on the cathode cycled in a full-cell without pre-cycling treatment. The performance of the control full-cell without pre-cycle treatment is very similar to the data shown in Figure 3a: low capacity, fast capacity fade and low Coulombic efficiency. More SEM and XPS characterization and discussion are in the Supporting Materials.

Excellent performance of full-cells with pre-cycled cathodes and anodes

The above discussion concludes that the pre-cycle treatment led to the preformation of SEI on both the $\text{Na}_{0.44}\text{MnO}_2$ cathode and the hard carbon anode and the SEI layers were stable in the following full-cell test. Hence, the problem of low Coulombic efficiency of electrodes can be circumvented, and the full-cell with both electrodes pre-cycled is expected to have a long cycle life. Figure 5 shows the optimized performance of $\text{Na}_{0.44}\text{MnO}_2$ -hard carbon full-cells with both cathodes and anodes pre-cycled in half-cells against Na metal. The full-cells were tested in the voltage window of 1.5 V to 4.1 V at 2C and 1C rates based on the cathode (1C = 120 mA/g). The cathode and anode were matched in a way targeting a high-energy full-cell battery with reasonably high power. The weight ratio between

the $\text{Na}_{0.44}\text{MnO}_2$ cathode and the hard carbon anode was $\sim 1:1$. Based on the half-cell performances (Figures 1 and 2), the corresponding capacity ratio between cathode and anode is $\sim 1:2$ at 0.5C rate (60 mA/g) based on the cathode, $\sim 1:1.5$ at 1C rate (120 mA/g), $\sim 1:1.1$ at 2C rate (240 mA/g), and $\sim 1:0.85$ at 4C rate (480 mA/g). The full-cell is cathode limited below 2C rate, yet it becomes anode limited at 4C rate.

Figure 5a presents the charge/discharge curves of a typical full-cell with features of sloped profiles and short plateaus from $\text{Na}_{0.44}\text{MnO}_2$. The charge/discharge curves have similar patterns over cycling even though the specific discharge capacity gradually decreases from ~ 108 to 83 mAh/g, based on the weight of $\text{Na}_{0.44}\text{MnO}_2$. Figure 5b shows the cycling data for the same full-cell in Figure 5a. Excellent long-term cycling stability with capacity retention of $\sim 77\%$ over 2000 cycles at 2C rate (240 mA/g) was obtained. The corresponding specific energy is ~ 280 Wh/kg based on $\text{Na}_{0.44}\text{MnO}_2$ weight (Figure 5c). The Coulombic efficiency at stable cycling is $>99.5\%$ and the energy efficiency is $\sim 93\%$.

Figures 5d-5f are the typical performance of a $\text{Na}_{0.44}\text{MnO}_2$ -hard carbon full-cell at 1C rate (120 mA/g). The charge-discharge curves have similar profile to that at 2C rate (240 mA/g) with an initial discharge capacity of ~ 116 mAh/g (Figure 5d). The Coulombic efficiency and energy efficiency are reasonably similar to those at 2C rate of $\sim 99.2\%$ and 93% , respectively. Yet the cycling stability drops greatly with capacity retention of $\sim 75\%$ over 1000 cycles (Figure 5e). The corresponding specific energy based on the cathode, however, increases to ~ 313 Wh/kg because of the specific capacity increase and voltage rise from the reduced polarization (Figure 5f). It is believed that the excess anode capacity (the capacity ratio between cathode and anode at 1C rate (120 mA/g) is $\sim 1:1.5$) and limited cycling stability of the hard carbon make the full-cell a bit distant from the optimum configuration.

The $\text{Na}_{0.44}\text{MnO}_2$ -hard carbon full-cell also has good rate performance. Figure S6 shows a full-cell with specific capacities of ~ 114 mAh/g at 0.1C rate (1C = 120 mA/g), ~ 111 mAh/g at 0.2C rate, ~ 109 mAh/g at 0.5C rate, ~ 106 mAh/g at 1C rate, ~ 102 mAh/g at 2C rate, and ~ 95 mAh/g at 4C rate. The capacity is ~ 107 mAh/g after testing for 40 cycles (5 cycles each at current densities of 0.1C, 0.2C, 0.5C, 1C, 2C,

and 4C, and 10 cycles at 0.5C), which demonstrates the ability of the full-cell to recover after being subjected to different charge/discharge rates. The full-cell has a poor long-term cycling stability at 4C rate because it is anode limited at such a high rate and the over-charging of the hard carbon anode brings a quick cell failure. Na metal deposition on the anode surface could be observed for $\text{Na}_{0.44}\text{MnO}_2$ -hard carbon full-cells after long-term cycling at 4C rate.

The effect of different operating voltage windows on full-cell performance also was investigated. Figure S7 shows a full-cell cycled between 1.5 and 3.8 V. The discharge capacity is ~ 95 mAh/g, which is ~ 13 mAh/g lower than that of the one cycled between 1.5 and 4.1 V (Figure S7a). The cycling stability is not affected by the cutoff voltage. The capacity retention over 2000 cycles at 2C rate (240 mA/g) is still $\sim 77\%$ (Figure S7b). Because of the low capacity and narrow voltage window, the specific energy (Figure S7c) is ~ 247 Wh/kg, $\sim 20\%$ less than that of the one operated between 1.5 and 4.1 V. Full-cells tested in a wider voltage window such as 1 to 4.5 V have a significant reduction in cycling stability because of the instability of electrolyte at high voltage.

It must be noted that the full-cell will have low capacity and poor cycling stability if either the cathode or anode surface layer is damaged during the disassembly of the pre-cycled half-cells or full-cell assembly. The goal for pre-cycling treatment of electrodes is to preform stable SEI layers on the electrode surfaces to reduce the consumption of Na ion stocks in full-cell cycling and hence achieve long stability. It allows us to bypass the complication introduced by the limited first-cycle Coulombic efficiency of the cathode and the anode, which greatly lowers specific energy and cycling stability of the full-cell. Damage of the surface layer usually leads to damage of the SEI layer and hence wastes the pre-cycle treatment.

Conclusion

In summary, we demonstrated the feasibility of long stability Na-ion battery full-cells. The model system of $\text{Na}_{0.44}\text{MnO}_2$ -hard carbon full-cell with pre-cycled electrodes has $\sim 77\%$ capacity retention over 2000 cycles at 2C rate. The critical role of a preformed intact SEI layer in achieving the best full-cell performance was elucidated, revealing that the low Coulombic efficiency of cathode and anode

materials is a major deficiency in the development of Na-ion battery full-cells. The $\text{Na}_{0.44}\text{MnO}_2$ -hard carbon full-cell chemistry is still distant towards satisfying the practical needs of Na-ion battery in many aspects. The pre-cycle treatment is not practical in industrial full-cell fabrication and also tricky to do in the lab. Nevertheless, our work helps pave the way for future development of Na-ion battery full-cells. Deployable Na-ion batteries with high energy density, high power, and low cost, not only need superior cathodes and anodes to further increase the specific energy and power and reduce the cost, but also require a stable electrolyte-electrode interface or SEI layer for high Coulombic efficiency. Currently, modification/functionalization of the surface of existing Na-ion battery cathode/anode materials, optimizing the electrolyte, or developing new stable high capacity cathode/anode materials of high Coulombic efficiency are primary approaches toward practical Na-ion battery technology.

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Appendix A. Supporting Information

Supplementary data associated with this article can be found in the online version.

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Figure Captions

Figure 1. Half-cell performance and structural stability of $\text{Na}_{0.44}\text{MnO}_2$. (a) Cycling performance of a typical $\text{Na}_{0.44}\text{MnO}_2$ half-cell between 2.0 and 3.7 V. The first 3 formation cycles were at 0.1C, and thereafter the rate was 1C for 2000 cycles. 1C = 120 mA/g. (b) Rate performance of a $\text{Na}_{0.44}\text{MnO}_2$ half-cell between 2.0 and 3.7 V. (c) HRTEM image and (inset) corresponding SAED pattern of pristine $\text{Na}_{0.44}\text{MnO}_2$. (d) STEM-HAADF image of pristine $\text{Na}_{0.44}\text{MnO}_2$. (e) HRTEM image and (inset) corresponding SAED pattern of $\text{Na}_{0.44}\text{MnO}_2$ after 1000 cycles. (f) STEM-HAADF image of $\text{Na}_{0.44}\text{MnO}_2$ after 1000 cycles. (g) Schematic view of the crystal structure of $\text{Na}_{0.44}\text{MnO}_2$ along the [010] axis. Gold spheres represent Na and pink spheres Mn. Oxygen was omitted for clarity.

Figure 2. Structure and half-cell performance of hard carbon. (a) XRD pattern of hard carbon. (b) A TEM image of hard carbon under low magnification. (c) A typical HRTEM image of hard carbon. (d) Selected charge-discharge curves of a typical hard carbon half-cell. (e) Cycling performance of the same half-cell in Figure 3d under various current densities.

Figure 3. Cycling performance of $\text{Na}_{0.44}\text{MnO}_2$ -hard carbon full-cells with electrodes having different pre-cycle treatments. (a) No pre-cycle treatment for either cathode or anode. (b) Only the hard carbon anode was pre-cycled. (c) Only the $\text{Na}_{0.44}\text{MnO}_2$ cathode was pre-cycled.

Figure 4. SEM and XPS characterization of hard carbon anodes and $\text{Na}_{0.44}\text{MnO}_2$ cathodes with or without pre-cycle treatment in full-cell tests. (a)-(b) SEM images of a pre-cycled hard carbon electrode and a hard carbon electrode cycled in a full-cell without pre-cycle treatment. (c) XPS C1s spectra of the same hard carbon electrodes in (a) and (b). (d)-(e) SEM images of a pre-cycled $\text{Na}_{0.44}\text{MnO}_2$ cathode and a $\text{Na}_{0.44}\text{MnO}_2$ cathode cycled in a full-cell without pre-cycle treatment. (f) XPS Mn2p spectra of the same $\text{Na}_{0.44}\text{MnO}_2$ cathodes in (d) and (e).

Figure 5. Electrochemical performance of $\text{Na}_{0.44}\text{MnO}_2$ -hard carbon full-cells with pre-cycled cathodes and anodes. (a) Selected charge-discharge curves of a typical full-cell at 2C rate (1C = 120 mA/g). (b) Cycling performance of the same full-cell in Figure 5a at 2C rate. (c) A plot of specific energy and energy efficiency vs. cycle number for the same full-cell in Figures 5a and 5b. (d) Selected charge-

discharge curves of another full-cell at 1C rate ($1C = 120 \text{ mA/g}$). (e) Cycling performance of the same full-cell in Figure 5d at 1C rate. (f) A plot of specific energy and energy efficiency vs. cycle number for the same full-cell in Figures 5d and 5e.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

TOC graphic

Recent personal portrait photo and a biosketch of authors

Dr. Xiaolin Li is a scientist at Pacific Northwest National Laboratory. He received his Ph.D. degree in 2005 from Department of Chemistry, Tsinghua University and conducted his postdoctoral research in Hongjie Dai's group at Stanford University. He has extensive experience with carbon nanotubes, graphene, and is an expert in designing nanostructured functional materials for various applications. His current research interest is on battery materials and renewable energy. He has authored/co-authored more than 40 papers, which have been cited for more than 17,000 times. His h-index is 45.

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Dr. Vincent Sprenkle joined PNNL in January 2001 and is currently Technical Group Manager for the Electrochemical Materials and Systems Group at PNNL. This group is focused on the development of electrochemical materials and systems for advanced energy storage and conversion applications. He is also currently project manager for the Department of Energy – Office of Electricity Energy Storage Program at PNNL. This project is focused on the development of electrochemical energy storage technologies to enable renewable integration and to improve grid support. He previously led other projects in the development of solid oxide fuel cell (SOFC) technology and planar Na batteries. Prior to his arrival at PNNL, he was a senior ceramic engineer at Litton Life Support and was responsible for the development of prototype advanced electrochemical oxygen generating system. Dr. Sprenkle currently holds 14 US patents on fuel cells, batteries, and high temperature electrochemical devices with 22 pending patent applications. He has been recognized as key contributor on 4 licensing activities while at PNNL and received a 2009 FLC award for Technology Transfer of Solid Oxide Fuel Cell Technology to Delphi Corporation.