Boosting Properties of 3D Binder-Free Manganese Oxide Anodes by Preformation of a Solid Electrolyte Interphase

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Huge irreversible capacity loss prevents the successful use of metal oxide anodes in Li-ion full cells. Here, we focus on the critical prelithiation step and demonstrate the challenge of electrolyte decomposition on a pristine anode in a full cell. Both an electrochemical activation process (54 h) with Li metal and a new electrolytic process (75 min) without Li metal were used to preform complete solid electrolyte interphase (SEI) layers on 3D binder-free MnO2-based anodes. The preformed SEI layers mitigated the electrolyte decomposition effectively and widened the working voltage for the MnO2/LiMnO2 full cell, which resulted in a big boost of the specific energy to 300 and 200 Wh kgcathe\textsuperscript{−1}, largely improved cycling stability, and much higher specific power (4200 Wh kg\textsubscript{f}\textsuperscript{−1}) compared to conventional Li-ion batteries. Detailed characterization, such as cyclic voltammetry, scanning transmission electron microscopy, and FTIR spectroscopy, gives mechanistic insight into SEI preformation. This work provides guidance for the design of anode SEI layers and enables the application of oxides for Li-ion battery full cells.

Introduction

Boosting the performance of electrode materials is considered as an attractive route to decrease Li-ion battery weight, volume, and cost. Significant achievements have been made in the research of cathode materials to replace toxic and costly LiCoO\textsubscript{2}, such as Li(Ni0.8Co0.1Al0.1)O\textsubscript{2}, Li(Ni0.5Co0.2Mn0.3)O\textsubscript{2}, modified LiMnO\textsubscript{2},[3] and LiFePO\textsubscript{4},[4] which are relatively cheap, environmentally acceptable, and already available for commercial application. Unfortunately, despite the extensive research on alternative anodes over the past 20 years, only a Sn/Co/C anode has been introduced to the market successfully by Sony, Japan, in 2005.[5] The use of Si/C hybrid nanostructures could also represent an effective solution to the foreseen limits of present anodes for Li-ion batteries provided that the cost of nanostructured Si can be forced down.[6] Meanwhile, a large number of metal oxide anodes (MO\textsubscript{y}M = Fe, Co, Ni, Mn, Sn, etc.)[7] with high capacities because of the conversion/deconversion reaction could be explored since the pioneering work of Tarascon et al.[8] These materials fulfill the needs for high capacity, wide availability, potentially low cost, and environmental friendliness. Particularly, nanostructured manganese oxides (MnO\textsubscript{y}) incorporated with carbon nanomaterials, such as carbon nanotubes (CNTs),[9] carbon nanofibers (CNFs),[10] and aligned carbon nanotubes (ACNTs),[11] and graphene,[12] delivered a large reversible capacity, good cyclic performance, and excellent rate capability in Li/MnO\textsubscript{y} half cells. Powerful and long-life Li-ion batteries could be achieved by using such MnO\textsubscript{y} anodes.

However, the evaluation of the electrochemical performance of the MnO\textsubscript{y} anode is always performed in the so-called “half-cell” configuration, in which the MnO\textsubscript{y} acts as a “cathode” with the Li metal as the counter electrode. In the Li/MnO\textsubscript{y} half cell with highly reactive Li metal, the reduction conditions of O2 and trace H2O and organic carbonates (ethylene carbonate (EC), diethylcarbonate (DEC), etc.)[13] and the following solid electrolyte interphase (SEI) formation are different from that in Li-ion full cells.

In particular, as other metal oxide anodes, MnO\textsubscript{y} anodes suffer from serious irreversible capacity loss (ICL) during the initial a few cycles in both the half and full cells. The main reasons for the ICL are understood to be caused by SEI formation and incomplete deconversion reaction.[14] For instance, the lithiation of the metal oxide anode could lead to the reductive decomposition of the electrolyte and form a thin SEI layer surrounded by a gel-like polymeric layer that can be dozens of nanometers thick, which coat the particles.[15] In addition, during the conversion reaction, strong structural reorganization takes place to accommodate the chemical changes and induces large volume changes, which results in severe particle decohesion and agglomeration.[16] The following deconversion reaction could be limited kinetically and incomplete. Thus, the Li ions are consumed to lead to the huge ICL.

To date, there are still relatively few studies on the application of metal oxides with a conversion reaction mechanism as anodes in Li-ion full cells. The groups of Tarascon[16,17] and Scrosati[18] reported the fabrication and testing of Li-ion full cells with CoO, and FeO\textsubscript{y} as anodes and with LiCoO\textsubscript{2}, LiMnO\textsubscript{2}, and LiFePO\textsubscript{4} as cathodes to give a working voltage of ~2 V.
a stable and reversible capacity of over 100 mA h g\textsuperscript{-1} (based on mass loadings of cathode). All the anodes needed to be activated electrochemically by Li/MO, half cells to mitigate the ICL before the full cell assembly. Recently, Chae et al.\textsuperscript{[20]} and Wang et al.\textsuperscript{[20]} reported full cells with prelithiated MnO\textsubscript{2} by a Li/MnO\textsubscript{2} half cell and LiMn\textsubscript{2}O\textsubscript{4} as the cathode to give a working voltage of ~3 V and a specific energy of ~300 Wh kg\textsuperscript{-1}. With the prelithiation, the highest reported value of 350 Wh kg\textsuperscript{-1} was achieved in a MnO\textsubscript{2}/LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} full cell.\textsuperscript{[21]} Therefore, the prelithiation of MO\textsubscript{2} is a critical step to boost the performances of such kinds of full cells. However, to the best of our knowledge, there is still a lack of detailed studies on the prelithiation of MO\textsubscript{2} and the exact mechanism of such an improvement is still not clear. Notably, Li metal can also react spontaneously with electrolyte to form the passive layer,\textsuperscript{[22]} which has a big influence on the prelithiation step. In addition, the use of Li metal involves process costs and poses a safety hazard because of the risk of short circuit, which could be difficult for the application on a large scale.

In this work, the electrochemical properties of our C/MnO\textsubscript{2}/ACNTs electrodes reported previously\textsuperscript{[23]} were studied in the Li/MnO\textsubscript{2} half cell and MnO\textsubscript{2}/LiMn\textsubscript{2}O\textsubscript{4} full cells. Such 3D binder-free electrodes offered an ideal view for the observation of the nanoparticle evolution after cycling.\textsuperscript{[20]} The influence of the binder on the SEI study was excluded.\textsuperscript{[24]} The challenge of the use of metal oxide anodes in the full cell was mainly a result of the electrolyte decomposition on the pristine surface, which was demonstrated clearly by comprehensive characterization studies. To solve this issue, two prelithiation methods with and without Li metal were used to preform the passive SEI layers. Firstly, a time-consuming (54 h) process activated electrochemically was applied to the pristine anode using a Li/MnO\textsubscript{2} half cell, which resulted in a big boost in the specific energy and cycling stability for the full cell. The full cell delivered a high specific energy of 223 Wh kg\textsuperscript{-1} (300 Wh kg\textsuperscript{-1}), 105 Wh kg\textsuperscript{-1} in just 4.5 min and a specific power up to 4200 Wh kg\textsuperscript{-1}, which is better than conventional Li-ion batteries. If we consider the limitations of the use of highly reactive Li metal, the influence of Li metal on the prelithiation step was excluded by the use of a new electrolytic cell, which was designed and fabricated by combining a Cu pitting corrosion type anodic half cell in aqueous electrolyte with a Li-ion battery type cathodic half cell in gel polymer electrolyte (GPE). With this electrolytic cell, the preformation of a complete SEI layer on the C/MnO\textsubscript{2}/ACNTs anode was achieved in just 75 min (2% of the time used for the previous process by Li/MnO\textsubscript{2} half cell). The full cell with a preformed SEI anode showed a big boost to the cycling performance, which was stable for 100 cycles. The initial output specific energy was 163 Wh kg\textsuperscript{-1} (200 Wh kg\textsuperscript{-1}), which was twice that for the full cell with a pristine anode. The effect of the preformed SEI layer was studied by systematic comparisons of different cells on the cycling stability, cyclic voltammetry (CV), and morphology changes of the C/MnO\textsubscript{2}/ACNTs and ex situ FTIR spectroscopy.

### Results and Discussion

#### MnO\textsubscript{2}/LiMn\textsubscript{2}O\textsubscript{4} Li-ion full cell with a pristine anode

The MnO\textsubscript{2}/LiMn\textsubscript{2}O\textsubscript{4} Li-ion full cell was tested in a three-electrode configuration (Figure 1). Nano-LiMn\textsubscript{2}O\textsubscript{4} with a uniform particle size distribution (~100 nm; Figure 2a) served as the cathode material for the full cell. The nano-LiMn\textsubscript{2}O\textsubscript{4} cathode delivered a good rate capability (93 mA h g\textsuperscript{-1} at 1200 mA g\textsuperscript{-1}), excellent cycling stability (12.5% fading after 1000 cycles), and high Coulombic efficiency (CE = 99.8%) in Li/LiMn\textsubscript{2}O\textsubscript{4} half cells (Figure S2). The excellent cycling stability and high CE of the nano-LiMn\textsubscript{2}O\textsubscript{4} cathode benefit the full cell performance.

![Figure 1. Schematic drawing of the MnO\textsubscript{2}/LiMn\textsubscript{2}O\textsubscript{4} Li-ion full cell.](image)

The C/MnO\textsubscript{2}/ACNTs electrode (Figure 2b) served as the anode for the full cell. In the Li/MnO\textsubscript{2} half cell, the C/MnO\textsubscript{2}/ACNTs electrode delivered high capacity (556 mA h g\textsuperscript{-1} at 0.5 C), excellent rate capability and cycling stability, and a high initial CE of 74.3% (Figure S3b), which is higher than most of the reported values.\textsuperscript{[25]} However, capacity fading was always observed after several hundred cycles (Figure S3c), the electrolyte was exhausted, and the Li metal surface was covered by a thick layer of powdery film without metallic luster (Figure S3c inset). The composition was confirmed by FTIR spectroscopy (see below). This indicated that the electrolyte degraded, and the solution products deposited on the Li metal surface continuously during long-term cycling. The electrolyte decomposition on the conversion-type metal oxide electrode has been verified by Li et al.\textsuperscript{[26]} They found that, unlike the intercalation-type materials, the huge volume expansion of the lithiated metal oxides tended to generate cracks in the SEI layer during the conversion reaction, which resulted in the continuous electrolyte decomposition.

![Figure 2. SEM images of a) nano-LiMn\textsubscript{2}O\textsubscript{4} and b) C/MnO\textsubscript{2}/ACNTs at low and high magnification (insets).](image)
Initially, the fresh nano-LiMn$_2$O$_4$ and pristine C/MnO$_2$/ACNTs electrodes were used directly as the cathode and anode, and a tiny Li metal wire served as the reference electrode to monitor the electrochemical potential variation of both electrodes during charge/discharge (Figure 1). All the MnO$_2$/LiMn$_2$O$_4$ full cells with C/MnO$_2$/ACNTs anodes showed a prolonged lithiation profile that started at the open-circuit voltage of the full cell $E_{oc}$ = 0.6 V. The nano-LiMn$_2$O$_4$ cathode worked well and had a potential plateau at around 4.1 V, which is the same as in the half cell. However, the potential of the C/MnO$_2$/ACNTs anode showed a prolonged lithiation profile that passed through the electrolyte reduction window, which is marked by red dashed line in Figure 3. The main reason for the lithiation slope is the well-understood reduction of the electrolyte that takes place on the pristine surface of C/MnO$_2$/ACNTs anode showed a prolonged lithiation profile that passed through the electrolyte reduction window, which is marked by red dashed line in Figure 3. The main reason for the lithiation slope is the well-understood reduction of the electrolyte that takes place on the pristine surface of C/MnO$_2$/ACNTs and ACNTs anode side, followed by the reaction with the Li$^+$ ions to form the SEI layer, which was verified by CV, scanning transmission electron microscopy (STEM), and FTIR spectroscopy (see below). A large amount of Li$^+$ ions was consumed, and the nano-LiMn$_2$O$_4$ cathode could not provide enough Li$^+$ ions for the further conversion reaction. Thus, the low CE led to a low initial discharge capacity of 33 mA h g$^{-1}$ (based on the total mass of nano-LiMn$_2$O$_4$ and C/MnO$_2$/ACNTs) and a low specific energy of 81 Wh kg$^{-1}$ for the full cell (Figure 3). Hence, the pristine C/MnO$_2$/ACNTs anode was not suitable for the full cell.

MnO$_2$/LiMn$_2$O$_4$ Li-ion full cell with an anode activated electrochemically by a Li/MnO$_2$ half cell

As in other full cell studies on the MnO$_2$ anode,$^{[19, 20]}$ in this work, one of the C/MnO$_2$/ACNTs anodes was cycled twice at a low current density (0.05 C) for 54 h for the formation of the SEI and discharged at 0.5 V vs. Li/Li$^+$ in the Li/MnO$_2$ half cell before the assembly of the full cell. Bright-field (BF) and dark-field (DF) STEM images of the C/MnO$_2$/ACNTs nanotube after the electrochemical activation by the half cell are shown in Figure 4. An SEI layer with a thickness of 3–10 nm covers the nanotube surface uniformly. The initial irreversible deconversion capacity was also compensated for during the two activation cycles, which resulted in a lower lithiation capacity for the activated anode compared to that of the pristine one. Hence, to balance the MnO$_2$/LiMn$_2$O$_4$ full cell, the c/a mass ratio was taken as 3 instead of 5 to avoid Li plating on the anode. The electrochemical potential variations of both electrodes and the voltage profiles for the full cell in the first cycle at C/6 and between 1.5 and 4.15 V are shown in Figure 5a. At the starting point of the initial charge, the potentials of the nano-LiMn$_2$O$_4$ cathode and C/MnO$_2$/ACNTs anode were 3.7 and 1.7 V vs. Li/Li$^+$, respectively, which correspond to the open-circuit voltage of the full cell $E_{oc}$ = 2.0 V. Then, the potential of the C/MnO$_2$/ACNTs anode decreased quickly and passed through the electrolyte reduction potential window in a short period, which is marked by the red dashed line in Figure 5a. The conversion reaction dominated the whole lithiation process for the C/MnO$_2$/ACNTs anode during the initial charge of the full cell. For the following discharge of the full cell, nearly 87.1 % Li$^+$ can be delithiated from the C/MnO$_2$/ACNTs anode during the deconver-
The full cell delivered an initial charge/discharge capacity of 340/296 mAh g

\(\text{C/MnO}_y/\text{ACNTs} \) (86/75 mAh g

\(\text{C/6} \)) and an average output voltage of ~3 V (Figure 5a). The charge/discharge capacities of the full cell at various current densities between 1.5 and 4.15 V are shown in Figure 5b. The full cell showed a good rate capability and delivered a charge/discharge capacity of 39 mA hg

\(\text{C/6} \) at 1 C, which was 52% of the value obtained at C/6. The discharge capacities with C rates of 2, 3, and 4 were 20, 10, and 6 mA hg

\(\text{C/6} \), respectively. The Ragone plot of the full cell is shown in Figure 5c. The specific energies and powers were calculated based on the total mass of active materials, and the state-of-art performances of Li-ion batteries (LIBs), Ni/MH batteries, and conventional supercapacitors (SCs) were estimated by Weng et al. [31]. At a low specific power of 146 Wkg

\(\text{C/6} \) total

\(^{-1} \), the full cell achieved a high specific energy of 223 Wh kg

\(\text{C/6} \) total

\(^{-1} \) (300 Wh kg

\(\text{C/6} \) cathode

\(^{-1} \) based on nano-LiMn

\(\text{C/6} \). Meanwhile, the specific energy of the full cell remained at 105 Wh kg

\(\text{C/6} \) if the specific power increased to 1400 Wkg

\(\text{C/6} \) total

\(^{-1} \), which was better than that of conventional Li-ion batteries. [32] The full cell can deliver a specific power up to 4200 Wkg

\(\text{C/6} \) total

\(^{-1} \) comparable to SCs, which is because both the 3D structured C/MnO/ACNTs anode and the nano-LiMn

\(\text{C/6} \) cathode offer fast charge transfer and matched well to each other at the high current density. The full cell showed also an improved cycling stability (Figure 5d). The full cell maintains ~80% of its initial capacity at C/6 after 20 cycles, but the capacity decays throughout cycling. The capacity retention is 50% at the 100th cycle with an average CE of ~98.5%. The improved electrochemical performance was mainly because of three reasons. First, the two activation cycles at 0.05 C helped the C/MnO/ACNTs anode to form a comparatively complete SEI layer. The preformed SEI layer avoided severe electrolyte decomposition and the following SEI growth for the full cell successfully, and Li ions were reserved for the further conversion/deconversion reaction. Second, after the activation cycles, the initial irreversible deconversion capacity of the C/MnO/ACNTs anode was compensated for by the Li/MnO

\(\text{C/6} \) half cell. Third, the initial electrochemical potential of the C/MnO/ACNTs anode was tuned downwards using the half cell, which widened the working voltage and boosted the specific energy for the full cell, as reported by Weng et al., [31] which had a similar effect on the graphene supercapacitor.

**Figure 5.** a) Electrochemical potential variation of both electrodes and voltage profile for the MnO/ LiMn

\(\text{C/6} \) full cell (c/a = 3) with the anode optimized electrochemically during the first cycle. b) Rate capability of the full cell at current densities of 1/6, 1, 2, 3, and 4 C (the full cell capacities were calculated based on the total mass of nano-LiMn

\(\text{C/6} \) and C/MnO/ACNTs). c) Ragone plot of the MnO/ LiMn

\(\text{C/6} \) full cell compared with other energy storage systems. d) Cycling stability of the MnO/ LiMn

\(\text{C/6} \) full cell at a current density of C/6 for 100 cycles.
reacts spontaneously with the reduction products, which makes the SEI preformation process difficult to control. The formation of a thick passive layer on the Li metal during the cycling of the Li/MnO₂ half cell (Figure S3c) also indicates that the recycling of the Li metal could be a knotty problem in practical applications. Furthermore, to explore the exact effect of the preformed SEI layer on the full cell performance, the influence of the highly reactive Li metal needs to be extracted. In the following section, a new electrolytic cell, in which the SEI layer of the C/MnO₂/ACNTs anode can be preformed in a rapid, well-controlled, and Li-metal-free process, will be presented and discussed.

The principle of our electrolytic cell is shown in Figure 6a. The electrolytic cell was designed and fabricated by combining a Cu pitting corrosion type anodic half cell in aqueous electrolyte with a Li-ion battery type cathodic half cell in a GPE. Recently, a similar creative setup has been proposed by Kim et al.,[33] namely, a metal-free hybrid seawater fuel cell. In our work, a Cu wire immersed in Li₂SO₄ aqueous solution was used as the counter electrode instead of the carbon paper immersed in Na-containing aqueous solution. The electrochemical mechanism of the electrolytic cell will be discussed below. A detailed description of this electrolytic cell is presented in the Experimental Section and Figure S1.

The CV curve of the electrolytic cell obtained using the cathodic half cell with the C/MnO₂/ACNTs electrode as working electrode, the anodic half cell with the Cu wires as counter electrode, and the Ag/AgCl as reference electrode from 0 to −4 V vs. Ag/AgCl (3.27 to −0.73 V vs. Li/Li⁺) at 1 mV s⁻¹ is shown in Figure 6b. In the initial cathodic process, a broad potential range between −1.4 and −2.5 V vs. Ag/AgCl (−1.9 to −0.7 V vs. Li/Li⁺) corresponds to the reduction of O₂ and trace H₂O₂, EC, DEC,[28] and high-valence Mn to Mn^{2+} on the working electrode. The cathodic current density increased from −2.5 V vs. Ag/AgCl, which is caused by the SEI formation. A peak at −3 V vs. Ag/AgCl (−0.3 V vs. Li/Li⁺) was attributed to the conversion reaction, that is, the formation of Li₂O and Mn⁴⁺. The intensity of the cathodic peak increased dramatically after the potential decreased from −3.3 V vs. Ag/AgCl (−0.73 V vs. Li/Li⁺), which was mainly because of the Li plating on the C/MnO₂/ACNTs electrode.[35] In the anodic process, the peak around −2.9 V vs. Ag/AgCl (−0.4 V vs. Li/Li⁺) might correspond to Li dissolution from the electrode.[35] The Mn⁴⁺ was reoxidized to Mn⁵⁺ at −1.6 V vs. Ag/AgCl (1.7 V vs. Li/Li⁺). A broad shoulder appeared gradually at −0.9 V vs. Ag/AgCl (2.3 V vs. Li/Li⁺) and merged with the main oxidation peak at −1.6 V vs. Ag/AgCl, which could be a result of the oxidation of Mn⁵⁺ to higher valence Mn. Both of the Mn oxidation peaks have an overpotential of −0.5 V compared to the CV curve of the Li/MnO₂ half cell,[36] which implies that the electrolytic cell suffered from polarization and that the reaction was limited kinetically because of the relatively long Li⁺ diffusion pathway in the electrolytic cell.

Meanwhile, pitting corrosion of Cu wires occurred in the anodic half cell (i.e., the oxidation of Cu wires from Cu⁰ to Cu⁷⁺) if the C/MnO₂/ACNTs electrode was reduced. In addition, the electrodeposition of soluble Cu⁷⁺ species in the anodic half

Figure 6. a) Principle of the SEI preformation on the C/MnO₂/ACNTs anode using our electrolytic cell with a Cu pitting corrosion type anodic half cell in aqueous electrolyte (0.5 M Li₂SO₄) and a Li-ion battery type cathodic half cell in GPE soaked in 1 M LiPF₆ EC/DEC (3:7 vol%). b) CV curve of the electrolytic cell obtained using the cathodic half cell with the C/MnO₂/ACNTs arrays on stainless steel as working electrode, the anodic half cell with the Cu wires as counter electrode, and Ag/AgCl as reference electrode from 0 to −4 V vs. Ag/AgCl (3.27 to −0.73 V vs. Li/Li⁺) at 1 mV s⁻¹. c) Galvanostatic profile for the SEI preformation of the C/MnO₂/ACNTs electrode at a current density of C/6 for 75 min using the electrolytic cell from −0.22 to −2.27 V vs. Ag/AgCl compared with the initial discharge curve of the Li/MnO₂ half cell from 2.8 to 0.5 V vs. Li/Li⁺.
cell occurred (i.e., the reduction of Cu$^{2+}$ from Cu$^{2+}$ to Cu$^{2+}$) if the C/MnO$_2$/ACNTs electrode was oxidized. Thus, the reaction for the anodic half cell is shown in Equation (1):

$$\text{Cu}^0 - 2e^- \rightarrow \text{Cu}^{2+}$$  \hspace{1cm} (1)

As we have reported previously, a Mn$_3$O$_4$ phase was found in the C/MnO$_2$/ACNTs sample. Based on the systematic work of Fang et al., during the initial cathodic step (in the high-potential range, Figure 6b) the total reaction of the electrolytic cell can be expressed as shown in Equation (2):

$$\text{Mn}_3\text{O}_4 + 2\text{Li}^+ + \text{Cu}^0 \rightarrow \text{Li}_2\text{O} + 3\text{MnO} + \text{Cu}^{2+}$$  \hspace{1cm} (2)

in parallel with the O$_2$ and H$_2$O trace, EC, and DEC reduction and SEI formation on the MnO$_x$ anode (Figure 6b). After all the Mn$_3$O$_4$ became MnO, the conversion reaction and Li plating happened [Eq. (3)]:

$$\text{MnO}(\text{sum}) + (2+x)\text{Li}^+ + (1+2x/2)\text{Cu}^0 \rightarrow \text{Li}_2\text{O} + \text{MnO} + x\text{Li}^2+ + (1+2x/2)\text{Cu}^{2+}$$  \hspace{1cm} (3)

for the following anodic CV process [Eq. (4)]:

$$y\text{Li}_2\text{O} + \text{MnO} + x\text{Li}^2+ + (y+x/2)\text{Cu}^0 \rightarrow \text{MnO}_y + (2y+x)\text{Cu}^0$$  \hspace{1cm} (4)

The main feature of the new cell is that it works as an electrolytic cell for the prelithiation of the C/MnO$_2$/ACNTs electrode through the reaction between the Cu metal and the Li salt, which are expensive and less available material, the c/a mass ratio was taken as 5. The electrochemical properties in the GPE were reserved to promote the reduction of the electrolyte followed by SEI formation, which consumed the Li$^+$ ions and resulted in the extra lithiation capacity.

The morphology of the preformed SEI C/MnO$_2$/ACNTs arrays was examined by SEM (Figure 7). The degree of alignment of the nanotubes and the pore morphology was maintained after SEI preformation compared to the fresh C/MnO$_2$/ACNTs array. However, agglomerates were observed among the nanotubes, and the surface of the arrays became smooth after the prelithiation (Figure 7a inset). The agglomerate might be because of the volume expansion of the lithiated MnO$_2$ nanoparticles, in addition to the preformed SEI and polymeric films. The BF-STEM image (Figure 7b) shows that the nanotubes were covered homogeneously by films, which could be attributed to the preformed SEI layer and a gel-like polymeric film. A small part of the CNT marked by blue lines in Figure 7c indicates the CNT coarsened in diameter from ~30 to 40–70 nm. So the thickness of the film was calculated to be 5–20 nm. However, for the C/MnO$_2$/ACNTs sample simply lithiated at 0.5 V vs. Li/Li$^+$ at C/6 by the Li/MnO$_2$ half cell (Figure 6c), the bare CNTs, nanoparticles, and some polymeric films are clear to see (Figure 7d), which means that the coating was not sufficient and the SEI layer was incomplete. In particular, some parts of the nanotube surface are still bare without any coating.

The preformed SEI C/MnO$_2$/ACNTs anode was then used in conjunction with the nano-LiMn$_2$O$_4$ cathode for the assembly of the MnO$_2$/LiMn$_2$O$_4$ full cell in the three-electrode configuration. For the full cell balancing and comparison with the pristine material, the c/a mass ratio was taken as 5. The electro-
chemical potential variation of both electrodes and the voltage profile for the full cell with the prelithiated anode during the first cycle at C/6 between 1.5 and 4.05 V are shown in Figure 8.

At the starting point of the initial charge, the potentials of the nano-LiMn$_2$O$_4$ cathode and C/MnO$_2$/ACNTs anode are 3.4 and 2.1 V vs. Li/Li$^+$, respectively, which corresponds to an open-circuit voltage of the full cell of $E_{oc} = 1.3$ V. The potential shoulder for the reduction of the electrolyte marked by the red dashed line is shorter than that of the full cell with a pristine anode (Figure 3). The conversion reaction dominated the whole lithiation process for the anode during the initial charge of the full cell. For the following discharge of the full cell, nearly 55.7% Li ions can be delithiated from the C/MnO$_2$/ACNTs anode, which is higher than the full cell with a pristine anode (c/a = 5, CE = 32.2%). The results also show an average discharge voltage of ~2.8 V and a charge/discharge capacity of 614/342 mA h g$^{-1}$ (102/57 mA h g$^{-1}$), based on the total mass of nano-LiMn$_2$O$_4$ and C/MnO$_2$/ACNTs; Figure 8 (Figure 8). The full cell delivered an initial output specific energy of 163 Wh kg$^{-1}$ at 95 Wh kg$^{-1}$, which is twice that of the full cell with a pristine anode. The reasons of the improved initial CE and increased specific energy should be similar to those for the full cell with a half-cell-activated anode (c/a = 3, CE = 87.1%) as described above. However, the conversion reaction did not occur in the electrolytic cell, thus the initial irreversible deconversion capacity was not compensated for, which resulted in a moderate initial CE value. Hence, further work still needs to be done to optimize the SEI preformation process through control of the lower cutoff potential for the electrolytic cell.

For a better comparison, the SEI-incomplete anode (Figure 7d) was also assembled into the MnO$_2$/LiMn$_2$O$_4$ full cell (c/a = 5). It delivered an initial CE of 53.2%, which was nearly the same as the full cell with the anode prelithiated by the electrolytic cell (Figure S6). However, the initial cycle is not enough to assess the full cell performance. Further comparison studies are presented below.

Effect of the preformed SEI layer on the MnO$_2$/LiMn$_2$O$_4$ full cell

The effect of the preformed SEI layer by using our electrolytic cell was studied by systematic comparison of different cells on the cycling stability, CV, morphology changes of the C/MnO$_2$/ACNTs, and ex situ FTIR spectroscopy.

Cycling stability

The discharge capacities of different full cells as a function of the cycle number at C/6 are shown in Figure 9a. The full cell with the preformed SEI anode delivered the best cycling performance that decreased from 56 mA g$^{-1}$ down to ~80% of its initial capacity in the first seven cycles. The decay of the capacity tended to stabilize over the next 93 cycles, which was similar to that observed using the previous half-cell activation. Severe capacity decay during the initial few cycles can also be found for other full cell studies that use metal oxide anodes.[19,21,40] The decay could be because of the continuous electrolyte decomposition and filling of the preformed SEI layer. After a few cycles, the defects of the SEI layer were filled, the electrolyte reduction reactions were difficult to perform for the solvent, and electrons were blocked by the SEI layer.[41] Hence, the full cell capacity stabilized after prolonged cycling.
However, the full cells with the pristine and SEI-incomplete anodes showed serious capacity fading of 81 and 63% after only 12 cycles, respectively. This indicated that the formation of a new SEI layer in the full cell did not self-passivate on the pristine C/MnO$_2$/ACNTs surface, which caused severe electrolyte decomposition and loss of Li ions. Hence, the preformation of a complete SEI layer is necessary for the C/MnO$_2$/ACNTs anode. The effect of the preformed SEI layer on the coulombic efficiency is shown in Figure 9b if the anode is coated with the preformed SEI layer by the electrolytic cell, the Coulombic efficiency of the full cell increased significantly from 55.8 to 97.2% in the initial 12 cycles and maintained a value of 98.5% in the following cycles. However, the Coulombic efficiencies of the full cells with the pristine and SEI-incomplete anodes only increased by 83.1 and 84.0% after 12 cycles, respectively. The cycling result also confirms that the SEI layer preformed by the electrolytic cell can effectively mitigate the electrolyte decomposition, prevent the charge loss, and improve the cycling stability for the MnO$_2$/LiMn$_2$O$_4$ full cell, which has a similar stabilizing effect as using the half cell for electrochemical activation.

**Cyclic voltammetry**

The CV analysis for the Li/MnO$_2$ half cell and the MnO$_2$/LiMn$_2$O$_4$ full cells with pristine and SEI anodes preformed using the electrolytic cell are shown in Figure 10. The CV curves were obtained using the C/MnO$_2$/ACNTs electrodes as the working electrodes, the Li metal (for half cell) or the nano-LiMn$_2$O$_4$ electrodes (for full cell) as the counter electrodes, and tiny Li metal wires as the reference electrodes at 0.1 mVs$^{-1}$. In the CV curve of the half cell (Figure 10a), a broad shoulder appeared gradually at 1.2 V vs. Li/Li$^+$ and merged with the main reduction peak at less than 0.3 V vs. Li/Li$^+$ in the first conversion process. The reaction current in the low-potential range between 0.5 and 0.1 V vs. Li/Li$^+$ was reduced in the second cycle because of the incomplete deconversion reaction and initial SEI formation.$^{[34]}$ Compared to the main reduction peak, the current density in the potential range between 2 and 0.7 V vs. Li/Li$^+$ was very low, which indicates that the electrolyte reduction was not severe. The oxidation peaks at 1.2 V vs. Li/Li$^+$ correspond to the deconversion reaction. In the CV curve of the full cell with the pristine anode (Figure 10b), two main broad reduction peaks that correspond to the electrolyte reduction and SEI formation were observed in the high-potential range (between 3 and 0.5 V vs. Li/Li$^+$) during the initial cathodic process. Moreover, unlike the CV curve of the half cell, there is no distinct peak at a low-potential range (<0.5 V vs. Li/Li$^+$). Hence, the conversion reaction was hindered, possibly caused by the exhaustion of Li ions or the particle coarsening because of run-away SEI formation. The following anodic current was very low, and the oxidation peaks shifted to 2.2 V vs. Li/Li$^+$, which indicated a strong polarization and poor reaction reversibility in this full cell. The reversibility of the MnO$_2$/LiMn$_2$O$_4$ full cell was improved remarkably by using the SEI anode preformed by the electrolytic cell (Figure 10c). The initial potential of the anode was decreased to 2 V vs. Li/Li$^+$ in the full cell. A broad reduction peak at ~1 V vs. Li/Li$^+$ was caused by the continuous electrolyte reduction and filling of the preformed SEI layer. The intensity of the cathodic peak increased dramatically after the potential decreased from 0.5 V vs. Li/Li$^+$, which was mainly caused by the conversion reaction. The deconversion reaction happened at ~1.3 V vs. Li/Li$^+$ in the following anodic process, which is the same as for the Li/MnO$_2$ half cell. These observations confirm that the preformed SEI layer compensated for the huge Li loss in the initial lithiation process and mitigated the electrolyte reduction and SEI formation to promote the conversion/deconversion reaction, and hence, improved the reversibility of total reaction for the full cell.

![Figure 10. CV profiles of a) Li/MnO$_2$ half cell and b) MnO$_2$/LiMn$_2$O$_4$ full cells with a pristine anode and c) preformed SEI anode using the electrolytic cell for the initial and second cycle at 0.1 mVs$^{-1}$. The C/MnO$_2$/ACNTs electrodes served as the working electrode, the Li metal (for half cell) or the nano-LiMn$_2$O$_4$ electrodes (for full cell) served as the counter electrodes, and the tiny Li metal wires served as the reference electrodes.](Image)
Morphology changes of the C/MnO_y/ACNTs after cycling

The changes of the morphology of the C/MnO_y/ACNTs samples in different cells were studied by STEM. All the samples were at the high-potential states (> 2.5 V vs. Li/Li^+) before the disassembly of the cells. The STEM images of the C/MnO_y/ACNTs samples cycled at 0.05 C twice and C/6 five times in the Li/ MnO_y half cell and full cells are shown in Figure 11. The sample cycled in the half cell maintained the degree of alignment of the nanotubes and the pore morphology (Figure 11a). There are no significant morphology changes compared to the uncycled sample (Figure 2b), although the nanotube surface became smoother and a thin, film-like structure can be observed in the BF-STEM image (Figure 11b), which could correspond to the SEI formation in the half cell. However, the pristine anode sample changed a lot after five cycles in the full cell (Figure 11c). The agglomerations are very significant, and the pore channels among the nanotubes are totally blocked, which makes it difficult to identify individual nanotubes. The surface of the agglomerates is rough. From the BF-STEM observation (Figure 11d), this agglomerate contains particles with bright color in the outer part, which is clearer in the DF-STEM image (Figure 11d, inset). The bright color particles could also be polymeric products. Unlike in the half cell,[39] not all of the polymeric products can be reoxidized and redissolve in the electrolyte in the full cell with a pristine anode. The polymeric residues are caused by the poor reaction reversibility as indicated by the CV results (Figure 10b). In addition, bare CNTs can be also found in the agglomerate (Figure 11d), which confirms that the pristine C/MnO_y/ACNTs could not form a self-passivating SEI layer in the full cell and causes continuous electrolyte decomposition in further cycling. For the preformed SEI anode sample, some nanotube structures can still be identified and the surface remains smooth (Figure 11e). No polymer-like particles or bare surfaces can be observed in the STEM images. However, the thickness of the coating layer on the nanotubes increased to 10–20 nm and the agglomerates coarsened (Figure 11f), which was mainly because the preformed SEI layer was filled during cycling.

Ex situ FTIR spectroscopy

As reported in anode studies with graphite[40] and Li metal,[22] FTIR spectroscopy can provide useful information on the composition on the particle surface. Ex situ FTIR spectroscopy [diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) mode] of the ACNTs, the powdery passive film on the Li metal after 700 cycles in the Li/MnO_y half cell, and C/MnO_y/ACNTs samples before and after various electrochemical processes are presented in Figure 12.

The pristine ACNTs (sample a) shows a typical FTIR spectrum of multiwalled carbon nanotubes (MWCNTs).[43] The peaks at ˜ν = 1708 and 1656 cm⁻¹ correspond to the C=O stretching vibrations of carboxyl functional groups. A band at ˜ν = 1534 cm⁻¹ together with a broadened peak at around ˜ν = 890 cm⁻¹ are attributed to the aromatic and unsaturated structure of C=C bonds, which resemble the graphite mode.[44] A band near ˜ν = 1415 cm⁻¹ is caused by C–O–C groups (oxides of structural, oxygen bridges, etc.).[45] A broad peak in the ˜ν = 1300–1100 cm⁻¹ region corresponds to the hydrated surface oxides (O–H deformation and C–O stretching vibrations).[45] All the ACNTs peaks are marked by black dashed lines and black numbers for the comparison of different spectra.

The FTIR spectrum of the powdery passive film on the Li metal anode surface after 700 cycles in the Li/MnO_y half cell (sample b) is also presented in Figure 12. The spectrum is similar to that for the EC reduction product[46] and the SEI on the graphite cycled in EC/DEC/1 M LiPF_6 electrolyte.[47] According to Aurbach et al.,[48] the peaks at approximately ˜ν = 1634, 1395, 1300, 1080, and 836 cm⁻¹ are attributed to ν_s(C=O), δ(CH_3), ν_l(C=O), ν(C–O), and δ(OOCO^−) deformations, respectively, which denote the existence of lithium ethylene dicarbonate (LEDc, CH_2COOCO_2Li). The peak at ˜ν = 1454 cm⁻¹ indicates the formation of Li_2CO_3 in this powdery film.[49] The other Li_2CO_3 peak at ˜ν = 880–860 cm⁻¹ is merged with the peak at ˜ν = 836 cm⁻¹. All the peaks attributed to the reduction of the electrolyte and the SEI layer are marked by red dashed lines and red numbers for the comparison of different spectra.
The unycled pristine \(\text{C/MnO}_y/\text{ACNTs}\) (sample c) shows nearly the same FTIR spectrum as the ACNTs, which could be a result of the homogeneous carbon coating on the \(\text{MnO}_y\) particles and the partially exposed ACNTs surface. After two cycles at 0.05 C and five cycles at C/6 in the Li/MnO\(_y\) half cell (sample d), all the ACNTs peaks disappeared and a distinct broad peak at \(\tilde{\nu} = 1080\ \text{cm}^{-1}\) was exhibited in the spectrum, which indicates that LEDC covered the \(\text{C/MnO}_y/\text{ACNTs}\) surface completely. However, for the pristine anode cycled five times at C/6 in the full cell (sample e), in addition to the LEDC peaks, a peak at \(\tilde{\nu} = 1454\ \text{cm}^{-1}\) is consistent with Li\(_2\)CO\(_3\). Moreover, a new strong peak is observed in the \(\tilde{\nu} = 850–700\ \text{cm}^{-1}\) region. This peak is associated with P–F stretching (\(\tilde{\nu} = 850–800\ \text{cm}^{-1}\)) and P–O–C (\(\tilde{\nu} = 830–740\ \text{cm}^{-1}\)) stretching in O–PF–OR compounds, and the P–F-containing species may originate from LiPF\(_6\) decomposition. This indicates that severe electrolyte decomposition and SEI formation occur in the full cell with a pristine anode, which is consistent with the above results.

For the uncycled preformed SEI anode using the electrolytic cell (sample f), the peak attributed to LiPF\(_6\) decomposition is even more pronounced, and the Li\(_2\)CO\(_3\) peak at \(\tilde{\nu} = 1454\ \text{cm}^{-1}\) can also be observed. No ACNTs peaks can be found in the spectrum, which also indicates that the preformed coating layer covered the \(\text{C/MnO}_y/\text{ACNTs}\) surface completely. The H\(_2\)O trace in the GPE of the electrolytic cell promoted the electrolyte and LiPF\(_6\) decomposition to form Li\(_2\)CO\(_3\), LiF, P–O–C, and P–F species, which provides enough species to form the complete initial SEI layer. The complete coverage of the SEI layer is consistent with the STEM observations (Figure 7). After five cycles in the full cell, the preformed SEI anode (sample g) shows no significant changes in the FTIR spectrum compared to the uncycled sample. The composition of the SEI layer was maintained after cycling, which indicates that the preformed SEI layer was comparatively stable and mitigated further electrolyte decomposition. Hence, the cycling stability of the full cell was improved. This is similar to that observed upon the addition of additional electrolyte decomposition products, such as Li\(_2\)CO\(_3\) into the electrolyte, which can suppress the ICL for the carbon anode. Actually, as long as 20 years ago, Ein Eli et al. found that a certain level of trace H\(_2\)O modified the surface chemistry of graphite anodes and improved the cycling stability of the graphite. However, trace H\(_2\)O consumes the Li ions and results in the ICL for the full cell with a pristine anode. Fortunately, these sacrificial Li ions can be compensated for by our electrolytic cell, and a better SEI layer design can be achieved by optimizing the SEI preformation process and adding SEI-formation improver and stabilizer (such as vinylene carbonate (VC), vinyl ethylene carbonate (VEC), Bu\(_4\)N, and organic borates) into the GPE in the electrolytic cell. The opposite deposition of such species on the highly reactive Li metal would not happen in the electrolytic cell.

For the SEI-incomplete anode prelithiated by the half cell (sample h), some ACNT peaks, such as the broad peak in the \(\tilde{\nu} = 1700–1500\ \text{cm}^{-1}\) region and the peaks at \(\tilde{\nu} = 1430\) and 890 cm\(^{-1}\) are still observed in the FTIR spectrum. After five cycles in the full cell, many new peaks appeared in the spectrum of the anode, which are attributed to the Li\(_2\)CO\(_3\), LEDC, and LiPF\(_6\) decomposition products. The composition of the SEI layer changed a lot, which indicates severe electrolyte decomposition and SEI formation, consistent with the above results.

**Conclusions**

Nano-LiMn\(_2\)O\(_4\) cathode materials and 3D binder-free \(\text{C/MnO}_y/\text{ACNTs}\) electrodes were synthesized successfully by the spontaneous reduction of permanganate ions with carbon. These electrodes delivered good electrochemical performances in the Li metal half cells. However, if the nano-LiMn\(_2\)O\(_4\)/ACNTs anode, a serious irreversible capacity loss occurred during the cycling for the full cells with various cathode/anode mass ratios. The challenges mainly result from the electrolyte decomposition on the pristine anode surface, which was demonstrated by cyclic voltammetry, scanning transmission electron microscopy, and FTIR spectroscopy. The use of the Li/MnO\(_y\) half cell to preform the solid electrolyte interphase (SEI) layer and mitigate the electrolyte decomposition and irreversible capacity loss is an effective but time-consuming approach (54 h). The full cell with the half-cell-optimized anode delivered
an initial output specific energy of 223 Wh kg\textsuperscript{-1} (300 Wh kg\textsuperscript{-1}, an initial Coulombic efficiency of 87.1%, and a largely improved cycling stability, which was stable for 100 cycles. In particular, the full cell can deliver 105 Wh kg\textsuperscript{-1} in just 4.5 min and a specific power up to 4200 Wh kg\textsuperscript{-1}, which is much better than that of conventional Li-ion batteries. However, if we consider the limitations of the use of highly reactive Li metal for the prelithiation, we demonstrated the concept of preforming the SEI layer on the pristine C/MnO\textsubscript{4}/ACNTs anode using a facile, cheap, Li-metal-free, and well-controlled method. An electrolytic cell was fabricated with a Cu pitting corrosion type anodic half cell in aqueous electrolyte and a Li-ion battery type cathodic half cell in gel polymer electrolyte. The initial SEI layer on the C/MnO\textsubscript{4}/ACNTs surface was preformed successfully in just 75 min by using this electrolytic cell. Without the Li metal, trace H\textsubscript{2}O and solution products in the gel polymer electrolyte were reserved and promoted the electrolyte reduction to form more SEI origins. The preformed SEI layer was more complete than that obtained by using the half cell at a high current of C/6. Thus, the SEI preformation time was shortened by 98% by using the electrolytic cell. The full cell with the preformed SEI anode also delivered a largely improved cycling stability with a similar stabilizing effect as the use of half-cell activation and an initial Coulombic efficiency of 55.7%, which was much better than the full cells with pristine and SEI-incomplete anodes. The initial output specific energy was 163 Wh kg\textsuperscript{-1} (200 Wh kg\textsuperscript{-1}) at 95 Wh kg\textsuperscript{-1}, which was twice that of the full cell with a pristine anode. The improved cycling stability and specific energy were mainly because of the preformed SEI layer that mitigated the electrolyte decomposition and widened the working voltage of the full cell. We believe that the strategy of the use of our electrolytic cell to boost the electrochemical performance of a Li-ion full cell is general and can be applied to other Li-ion anodes and optimized SEI layers.

**Experimental Section**

**Material synthesis**

**Preparation of C/MnO\textsubscript{4}/ACNTs anode**

As we reported previously\textsuperscript{[1]} stainless-steel foil (Alfa Aesar, Type 304, 25 μm) was cut into circular discs with a diameter of 14 mm. The ACNTs were synthesized directly on the stainless-steel foil by using a one-step floating catalyst method.\textsuperscript{[31]} The MnO\textsubscript{2} was applied to the ACNTs through the spontaneous reduction of KMnO\textsubscript{4} (Sigma–Aldrich, 99.0%) by carbon. The carbon coating was performed in a quartz reactor using chemical vapor deposition (CVD) in a C\textsubscript{2}H\textsubscript{2} atmosphere. The weight of the C/MnO\textsubscript{4}/ACNTs was calculated by subtracting the weight of stainless-steel foil from the total weight of the electrode. A typical loading of C/MnO\textsubscript{4}/ACNTs was 0.5–1 mg cm\textsuperscript{-2}. The mass ratio of MnO\textsubscript{2} in the C/MnO\textsubscript{4}/ACNTs composite is ~60% (see Supporting Information for details).

**Preparation of nano-LiMnO\textsubscript{4}**

Commercial MWCNTs were dispersed in 65 vol.% HNO\textsubscript{3} for 2 h with sonication to remove some impurities and endow the surface with hydrophilic groups such as –OH and –COOH.\textsuperscript{[24]} The LiMnO\textsubscript{4} solution was prepared by dissolving KMnO\textsubscript{4} (20 g; Sigma–Aldrich, 99.0%) in distilled water (100 mL) at 60°C, followed by the addition of LiO\textsubscript{2} (14 g; Sigma–Aldrich, >95.0%) into the KMnO\textsubscript{4} solution under vigorous stirring. The mixture was poured into a beaker in an ice bath. Then the mixture was filtered five times to remove the KClO\textsubscript{4} precipitation. The filtrate was diluted with distilled water to prepare a ~0.01 m LiMnO\textsubscript{4} solution for the subsequent coating process. The as-prepared MWCNTs (0.1 g) and H\textsubscript{2}SO\textsubscript{4} (50 μL; Sigma–Aldrich, 95.0–98.0%) were added into the LiMnO\textsubscript{4} coating solution (100 mL), and the solution was kept at 85°C for 1 h. A hybrid Li/MnO\textsubscript{4} coating on MWCNTs was obtained. The obtained materials were milled with LiOH·H\textsubscript{2}O (Sigma–Aldrich, 99.0% in ethanol (10 mL). The mixture was sonicated for 1 h followed by drying in a fume hood and calcination at 700°C for 8 h in air to obtain nano-LiMnO\textsubscript{4} with good crystallinity.

**Material characterization**

The crystal structure of nano-LiMnO\textsubscript{4} was analyzed by XRD using CuK\textsubscript{α} radiation (Bruker AXS D8 FOCUS diffractometer with a LynxEye PSD). The morphologies of the nano-LiMnO\textsubscript{4} and C/MnO\textsubscript{4}/ACNTs composites were studied using scanning (transmission) electron microscopy (S(T)EM, Hitachi S-5500). To investigate any changes in the morphology of the C/MnO\textsubscript{4}/ACNTs electrode, the samples were characterized by STEM also after various electrochemical processes. The surface composition of the ACNTs and C/MnO\textsubscript{4}/ACNTs composites were studied qualitatively using FTIR spectroscopy in the DRIFTS mode ( Nicolet iS50 FT-IR Spectrometer). To investigate any composition changes on the surface of the C/MnO\textsubscript{4}/ACNTs electrode, the samples were characterized by FTIR spectroscopy also after various electrochemical processes. The detailed sample preparation procedures are presented in the Supporting Information.

**Half-cell studies**

The LiMnO\textsubscript{4} cathode was prepared by mixing 68 wt.% of the nano-LiMnO\textsubscript{4} with 23 wt.% Supper-P carbon black (Alfa Aesar, >99%) and 9 wt.% poly(vinylidene fluoride) (PVDF; Kynar, reagent grade). A slurry was made by ball milling, using N-methyl-2-pyrroli- dene (NMP; Sigma–Aldrich, >99%) as the solvent. The electrodes were formed by tape casting the slurry onto Al foil, followed by drying overnight at 90°C in a vacuum furnace. The electrode was cut into circular discs with a diameter of 14 mm and a typical cathode loading of 2–5 mg cm\textsuperscript{-2}. Both the nano-LiMnO\textsubscript{4} cathode and the C/MnO\textsubscript{4}/ACNTs electrode were assessed by using 2016 coin cells, using lithium metal as the anode and a Celgard 2400 film as the separator. The electrolyte used was 1 m LiPF\textsubscript{6} (Aldrich, ≥99.99%) dissolved in EC (Sigma, 99%)/DEC (Aldrich, ≥99%) (3:7 volume ratio). Cell assembly was performed in an Ar-filled glove box, in which the water and oxygen concentrations were 0.1 ppm. Charge/discharge analysis was performed galvanostatically by using an eight-channel battery analyzer (MTI corporation, USA) at RT (~20°C).

**Full cell studies**

Before the full cell studies, all the electrodes and cell components were dried in a vacuum oven at 100°C for 12 h and kept for 24 h inside the Ar-filled glovebox to make sure the H\textsubscript{2}O and O\textsubscript{2} residues were as low as possible. The MnO\textsubscript{2}/LiMnO\textsubscript{4} full cell with the nano-LiMnO\textsubscript{4} cathode and C/MnO\textsubscript{4}/ACNTs anode was assembled by
using a two-electrode cell (EL-CELL ECC-Ref Electrochemical Test Cell, Germany) with a reference electrode holder that can be loaded with a tiny Li metal wire. The electrolyte used was also 1 M LiPF$_6$ EC/DEC (3:7 volume ratio), and the separator was a Celgard 2400 film. The MnO$_2$/LiMnO$_2$ full cell was charged and discharged in the two-electrode configuration between 1.5 and −4.1 V vs. Li/Li$^+$. By using an eight-channel battery analyzer (MTI corporation, USA) at −20 °C. The upper voltage limit of the full cell was determined by when potential of the nano-LiMnO$_2$ cathode reached 4.3 V vs. Li/Li$^+$. The lower limit was determined when the potential of the C/MnO$_2$/ACNTs anode reached 0.1 V vs. Li/Li$^+$. The current densities were calculated based on the mass loading of the C/ MnO$_2$/ACNTs anode (1 C = 1200 mA g$_{C/MnO_{2}/ACNTs}^{-1}$). The optimized $c$/a ratio was determined by the highest initial CE and specific discharge capacity of the full cell. In this work, all the optimized $c$/a values were 5, except the full cell with the activated anode ($c/a = 3$). CV of the full cell was performed at a scan rate of 0.1 mVs$^{-1}$ by using a potentiostat (Princeton VersaSTAT, USA). The C/MnO$_2$/ ACNTs anode served as the working electrode, the nano-LiMnO$_2$ cathode or Li metal (for half cell) served as the counter electrode, and the tiny Li metal wire served as the reference electrode.

**Electrolytic cell studies**

The electrolytic cell is shown schematically in Figure S2. The full cell consists of the cathodic and anodic half cells. The cathodic half cell is composed of a steel cap with an open circle in the middle. The cap surface was covered by a layer of glass to make the cap waterproof and insulating. A LISICON film covered the open area with an epoxy seal between the LISICON film and the cap. The LISICON film (Ohara GmbH, Germany), which consists of Li$_2$O-Al$_2$O$_3$, SiO$_2$-P$_2$O$_5$-TiO$_2$-CeO$_2$, has a thickness of 150 μm, a high Li$^+$ conductivity of 0.1 mS cm$^{-1}$[31] and a high seawater stability of > two years (evidenced by past evaluations at Polyplus Battery company). The cathodic half cell was dried in purified air. The assembly of the cathodic half cell of the electrolytic cell was performed in an Ar-filled glovebox. After drying, the C/MnO$_2$/ACNTs electrode was placed inside the cathodic half cell and covered by a GPE. The GPE was made by saturating a dried sandwiched polymer membrane (poly(vinyl difluoride) (PVDF; Kynar, reagent grade)/poly(methyl methacrylate) (PMMA; Aifa Aesar, Mw = 61 000)/PVDF[30] dried in a vacuum at 60 °C) of 100 μm with 1 M LiPF$_6$ EC/DEC (3:7 vol% electrolyte). The cathodic half cell was taken out of the glovebox and assembled with the anodic half cell to make the electrolytic cell.

The anodic half cell was composed of a glass electrolytic tank filled with the Li-containing aqueous solution (0.5 M Li$_2$SO$_4$: Sigma–Aldrich, 99.0%) and an anticorrosion Ti stick wrapped with Cu wires, which were polished to remove the enamel coating. Thus, the Cu surface was exposed to the aqueous solution for the electrochemical corrosion. A reference electrode of Ag/AgCl was placed in the electrolytic tank.

CV of the electrolytic cell was performed at a scan rate of 1 mVs$^{-1}$ by using a potentiostat (Princeton VersaSTAT, USA) with the C/ MnO$_2$/ACNTs electrode as working electrode, the Cu wires as counter electrode, and the Ag/AgCl as reference electrode. The galvanostatic preformation of the SEI layer on the C/MnO$_2$/ACNTs electrode was performed at a current of C/6 (200 mA g$_{C/MnO_{2}/ACNTs}^{-1}$) by using the same potentiostat. After the prelithiation process, the electrolytic cell was disassembled. The cap top of the cathodic half cell was washed with distilled water following by drying in purified air. Then, the cathodic half cell was transferred to the glovebox and disassembled. The preformed SEI C/MnO$_2$/ACNTs electrode was taken out from the cathodic half cell to assemble the MnO$_2$/ LiMnO$_2$ full cell.

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