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## A hybrid electrolyte energy storage device with high energy and long life using lithium anode and MnO<sub>2</sub> nanoflake cathode

### Abstract

A hybrid electrolyte energy storage system combining the features of supercapacitors and lithium batteries has been constructed. It consists of MnO<sub>2</sub> nanoflakes in 1 M Li<sub>2</sub>SO<sub>4</sub> aqueous electrolyte as the cathode and lithium foil in ionic liquid (1 M lithium bis(trifluoromethanesulfonyl)imide (LiNTf<sub>2</sub>) in N-methyl-N-propyl pyrrolidinium bis(trifluoromethanesulfonyl)imide ([C(3)mpyr][NTf<sub>2</sub>])) electrolyte as the anode, separated by a lithium super ionic conductor glass ceramic film (LiSICON). This system shows the advantages of both a supercapacitor (long cycle life) and a lithium battery (high energy), as well as low cost and improved safety due to the combination of ionic liquid and ceramic solid state electrolyte in lithium side, which can reduce the formation and prevent the penetration of lithium dendrites. The specific energy for the cathode materials in the hybrid electrolyte system is 170 Wh kg<sup>-1</sup> with more than 85% retention up to 2400 cycles. This system is a great candidate for stationary batteries storing solar and wind energy. (c) 2013 Elsevier B.V. All rights reserved.

### Keywords

mno<sub>2</sub>, anode, lithium, life, long, high, cathode, device, nanoflake, storage, energy, electrolyte, hybrid

### Disciplines

Engineering | Physical Sciences and Mathematics

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# A Hybrid Electrolyte Energy Storage Device with High Energy and Long Life using Lithium Anode and MnO<sub>2</sub> Nanoflake Cathode

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KEYWORDS: Hybrid electrolyte; Supercapacitor; Lithium battery; High energy; MnO<sub>2</sub>; ionic liquid; LiSICON.

**ABSTRACT:** A hybrid electrolyte energy storage system combining the features of supercapacitors and lithium batteries has been constructed. It consists of MnO<sub>2</sub> nanoflakes in 1 M Li<sub>2</sub>SO<sub>4</sub> aqueous electrolyte as the cathode and lithium foil in ionic liquid (1 M lithium bis(trifluoromethanesulfonyl)imide (LiNTf<sub>2</sub>) in *N*-methyl-*N*-propyl pyrrolidinium bis(trifluoromethanesulfonyl)imide ([C<sub>3</sub>mpyr][NTf<sub>2</sub>])) electrolyte as the anode, separated by a lithium super ionic conductor glass ceramic film (LiSICON). This system shows the advantages of both a supercapacitor (long cycle life) and a lithium battery (high energy), as well as low cost and improved safety due to the combination of ionic liquid and ceramic solid state electrolyte in lithium side, which can reduce the formation and prevent the penetration of lithium dendrites. The specific energy for the cathode materials in the hybrid electrolyte system is 170 Wh kg<sup>-1</sup> with more than 85% retention up to 2400 cycles. This system is a great candidate for stationary batteries storing solar and wind energy.

## Introduction

The market for global clean energy, including both solar photovoltaics and wind power, for example, has grown by more than 20 times during the past decade from \$7.6 billion in 2001 to \$163.1 billion in 2011, according to Clean Edge's *Clean Energy Trends* report [1]. The effective use of clean energy is a great challenge to researchers due to its discontinuous availability, depending on both time and weather conditions. Therefore, how to store the discontinuous electric current is the key point. The battery systems proposed for the storage of clean energy include lead acid [2], nickel/cadmium [3], vanadium-redox flow [4], and sodium/sulfur batteries [5,6]. For the first three systems, the biggest concern is the toxic materials involved in those systems in terms of the impact on the environment. For the sodium/sulfur batteries, the high operating temperature ( $\sim 350$  °C) is the major disadvantage [7].

Although rechargeable lithium-ion batteries (LIBs) have been successfully used in portable electronic devices, such as cell phones, cameras, and laptop computers since 1991, when they were introduced by Sony [8], the LIBs need to be further developed to meet the requirements for use as an energy storage system to store clean energy [9]. The volumetric energy density is not that crucial, due to the fact that the energy storage system will be stationary and won't need to be moved very often. The essential requirements of an energy storage device for storing clean energy are low cost, long cycle life, and safety.

Supercapacitors can normally achieve a high cycling performance, but with relatively low energy density [10]. For example, supercapacitors based on  $\text{MnO}_2$  active materials in aqueous electrolyte can be cycled up to 30,000 cycles with capacity retention higher than 80%, but the energy density is less than 10% of the energy density of LIBs [11].

On the other hand, lithium metal shows great advantages as the anode material for lithium batteries, such as high theoretical capacity ( $\sim 3800 \text{ mAh g}^{-1}$ ) and highly reversible capacity. This has been known since the late 1970s [12]. The commercialization of the lithium metal battery was not successful, however, due to the safety issues related to the lithium dendrites that grow during cycling. Room temperature ionic liquids (RTILs), which are flame resistant, non-volatile, and electrochemically stable, can effectively prevent the formation of lithium dendrites, showing potential as safe electrolytes in lithium battery systems [13-15]. Recently, superionic conductor glass ceramic film (LiSICON) was also proposed as an ionic conducting electrolyte and/or separator for preventing the penetration of lithium dendrites during cycling [16,17]. Novel lithium hybrid electrolyte systems have been proposed by Zhou's group [18-21] and Goodenough's group [22] using Cu,  $\text{Ni(OH)}_2$ , and water-soluble redox couple solutions as cathode. Recently, Makino et. al. reported that the hybrid EC ( $\text{Li} \mid \text{PEOLiTFSI} \mid \text{LTAP} \mid 1.0 \text{ M Li}_2\text{SO}_4 \text{ aq.} \mid \text{MnO}_2$ ). However, there is no cycling results shown. The specific charge calculated from the discharge curve at  $0.255 \text{ mA cm}^{-2}$  was only  $31.4 \text{ mAh g}^{-1}$  based on  $\text{MnO}_2$ , which translates to specific energy of  $114 \text{ Wh kg}^{-1}$  [23]

Here, we propose a hybrid electrolyte system combining the features of supercapacitors and lithium batteries that uses  $\text{MnO}_2$  nanoflakes in  $1 \text{ M Li}_2\text{SO}_4$  aqueous electrolyte as the cathode and lithium in  $1 \text{ M}$  lithium bis(trifluoromethanesulfonyl)imide ( $\text{LiNTf}_2$ ) in *N*-methyl-*N*-propyl pyrrolidinium bis(trifluoromethanesulfonyl)imide ( $[\text{C}_3\text{mpyr}][\text{NTf}_2]$ ) electrolyte as the anode, separated by a LiSICON solid state electrolyte, as shown in Figure 1. This system has several advantages: 1) long cycle life, because of the excellent cycle life of  $\text{MnO}_2$  in aqueous electrolyte supercapacitors, as reported previously [11,24,25]; 2) higher specific energy, as the working voltage ( $3.4 \text{ V}$ ) is almost 6 times higher than that of aqueous based supercapacitors; 3) improved

safety due to the combination of ionic liquid and ceramic solid state electrolyte in lithium side, which can reduce the formation and prevent the penetration of lithium dendrites; 4)  $\text{MnO}_2$  as the active material, which is cheap and environmentally friendly.

## Experimental section

The lithium was sealed in a bottle cell with LiSICON as the window inside of an Mbraun Ar-filled glove box. The lithium side electrolyte is 1 M lithium bis(trifluoromethanesulfonyl)imide ( $\text{LiNTf}_2$ ) (Sigma-Aldrich) in *N*-methyl-*N*-propyl pyrrolidinium bis(trifluoromethanesulfonyl)imide ( $[\text{C}_3\text{mpyr}][\text{NTf}_2]$ ) (TCI America). The LiSICON ( $\text{Li}_{1+x+3z}\text{Al}_x(\text{Ti,Ge})_{2-x}\text{Si}_{3z}\text{P}_{3-z}\text{O}_{12}$ ) was purchased from Ohara Inc., Japan and had a thickness of 150  $\mu\text{m}$ . The  $\text{MnO}_2$  nanoflakes were prepared via similar electrochemical deposition to that previously reported [24,25]. The amount deposited can be controlled in a range of 0.05 to 0.2  $\text{mg cm}^{-2}$ . The mass of  $\text{MnO}_2$  can be obtained by weighting the substrate before and after electrochemical deposition. The  $\text{MnO}_2$  side electrolyte is 1 M  $\text{Li}_2\text{SO}_4$  in de-ionized (DI)-water. Electrochemical measurements including cyclic voltammetry (CV) and constant current charge-discharge curves were obtained from a Biologic VMP-3 electrochemical workstation using both a 2-electrode system and a 3-electrode system at 25  $^\circ\text{C}$ , respectively. The reference electrode used in the 3-electrode system is Ag/AgCl in 3M KCl solution on the  $\text{MnO}_2$  side. The specific capacity is based on the weight of  $\text{MnO}_2$  on the stainless steel mesh.

## Results and Discussion

Cyclic voltammetry (CV) curves measured in the 3-electrode system are presented in Figure 2. Figure 2(a) shows a CV curve collected with a slow scan rate of 1  $\text{mV s}^{-1}$ . The two small redox peaks at 0.49 V and 0.63 V can be assigned to the lithium insertion and de-insertion into  $\text{MnO}_2$ ,

respectively [26]. When the scan rate was increased to  $20 \text{ mV s}^{-1}$ , the CV curve changed to a square shape, which is the typical supercapacitor feature [27-29]. The specific capacitance can be calculated from the CV curves using  $C = I/mV$ , where  $C$  ( $\text{F g}^{-1}$ ) is specific capacitance,  $I$  (A) is the average current value in CV curves,  $m$  (g) is the weight of active materials,  $V$  ( $\text{V s}^{-1}$ ) is the scan rate. The specific capacitance calculated from the CV curves is 232 and  $150 \text{ F g}^{-1}$  for scan rates of  $1 \text{ mV s}^{-1}$  and  $20 \text{ mV s}^{-1}$ , respectively. The data is matched very well with our previous report on the aqueous supercapacitor system [11,24,25].

The charge and discharge curves in the 3-electrode system are presented in Figure 3. The potential variations of both the cathode and anode versus the reference electrode (RE) can be monitored. Therefore, the charge and discharge curves shown in Figure 3a) and 3b) are plotted versus RE and the counter (Li) electrode, respectively. The charge and discharge curves are typical supercapacitor sloping curves. The specific capacitance and capacity are  $230 \text{ F g}^{-1}$  and  $50 \text{ mAh g}^{-1}$ , which are similar to the results in a previous report [24,25]. The average working potential is  $3.4 \text{ V}$  which is a 1.7 times higher than that of the aqueous system ( $\sim 2 \text{ V}$ ). The specific energy for the cathode materials in the hybrid electrolyte system is  $170 \text{ Wh kg}^{-1}$ , which is also more than 50% higher than that reported in ref [23]. The current density used here is  $50 \text{ mA g}^{-1}$ , which is equal to the 1 C rate.

IR drop can be observed during the discharge process in the 2-electrode system. To further investigate the IR drop, different current densities were also used to charge and discharge the 3-electrode system cell. The different current densities used include 50, 100, 200, and  $500 \text{ mA g}^{-1}$ , and the discharge curves are shown in Figure 3c) and 3d). It can be found that the IR drop referring to the reference electrode is much smaller than that referring to the lithium electrode. Moreover, the IR drop is also increased significantly for discharge curves referring to the lithium

electrode when the current density is increased. This is due to the fact that the ionic conductivity of LiSICON is much smaller than that of 1 M Li<sub>2</sub>SO<sub>4</sub> in water. From Fick's second law,

$$D = L^2/t,$$

where D is the lithium diffusion coefficient ( $10^{-8}$  -  $10^{-9}$  cm<sup>2</sup> s<sup>-1</sup>) [30], L is the thickness of the LiSICON film (0.015 cm), and t is the diffusion time. The calculated diffusion time is in the range of 6.2 to 62.5 h. Therefore, the lithium ions need about 60 h to diffuse from one side to another. Both the low ionic conductivity and the low lithium diffusion coefficient are the reason for the large IR drop.

The charge and discharge curves in the 2-electrode system are shown in the inset of Figure 4. The IR drop in the two electrode system is much higher than in the 3-electrode system. This has also been observed in other hybrid electrolyte systems [18-21,23]. The possible reason is that the solid electrolyte has a low lithium diffusion coefficient, which limits the rate capability of this system. The IR drop can be minimized by improving the cell design, such as by increasing the area and decreasing the thickness of the solid state electrolyte. The 1 C rate is already capable of storing and delivering charge efficiently in most cases relevant to renewable energy storage. The cycle life of the hybrid electrolyte Li-MnO<sub>2</sub> system is shown in Figure 4. Up to 2400 cycles can be achieved at the 1 C rate, and the capacity drop is less than 15 %.

## **Conclusion**

We have demonstrated a hybrid electrolyte system (lithium-ionic liquid || LiSICON || aqueous electrolyte-MnO<sub>2</sub>) with advantages of both a supercapacitor (long cycle life) and a lithium battery (high energy). The system showed great advantages, including long cycle life, low cost, safety,

and relatively good energy density and rate capability. This system could be a great candidate for stationary batteries storing solar and wind energy.

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Figure Captions

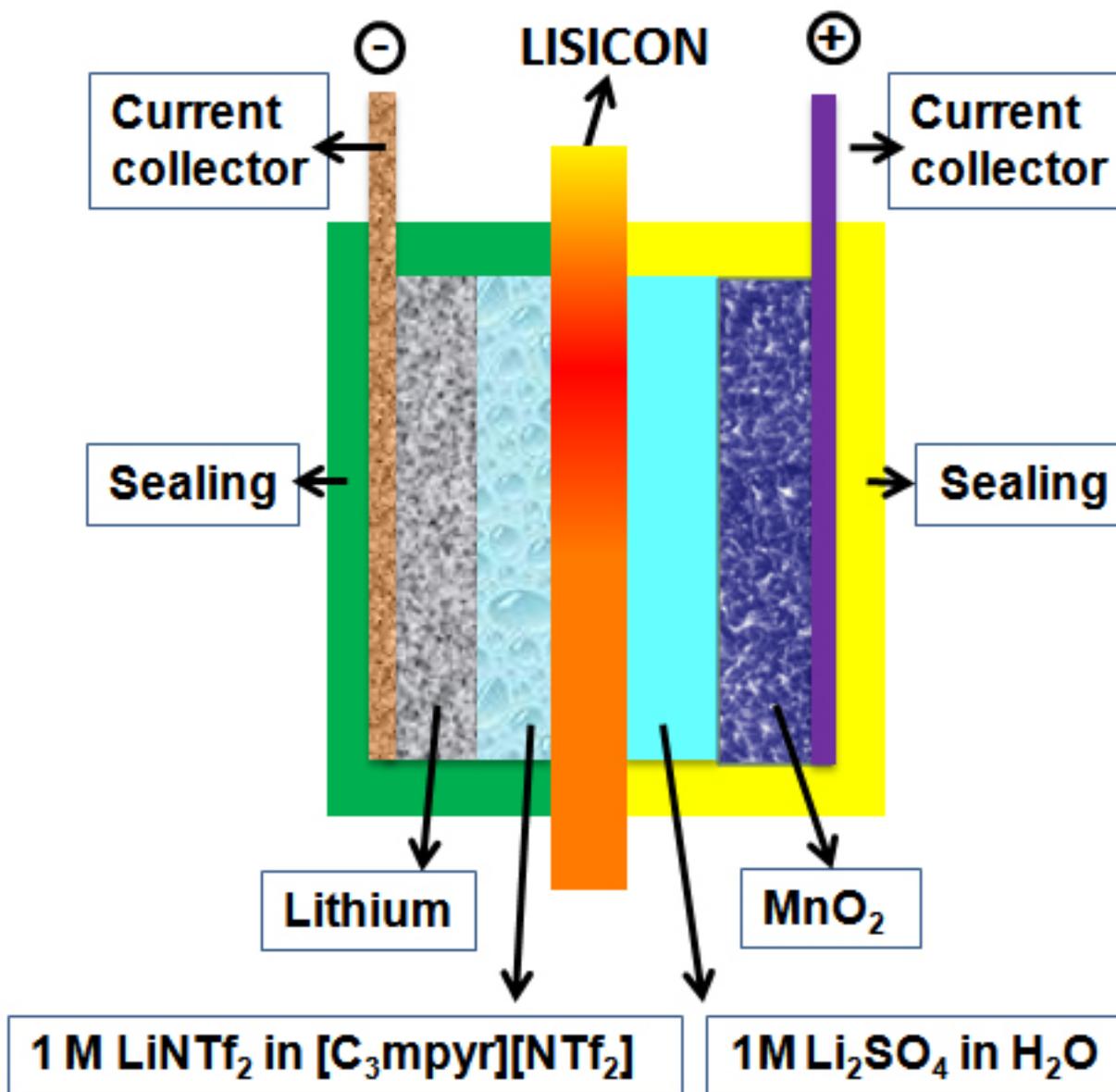
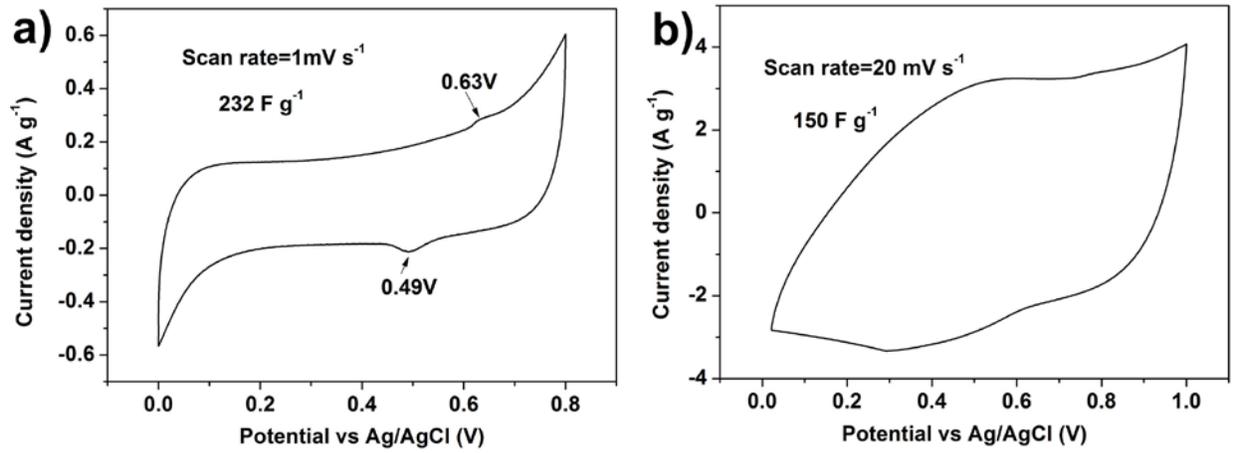
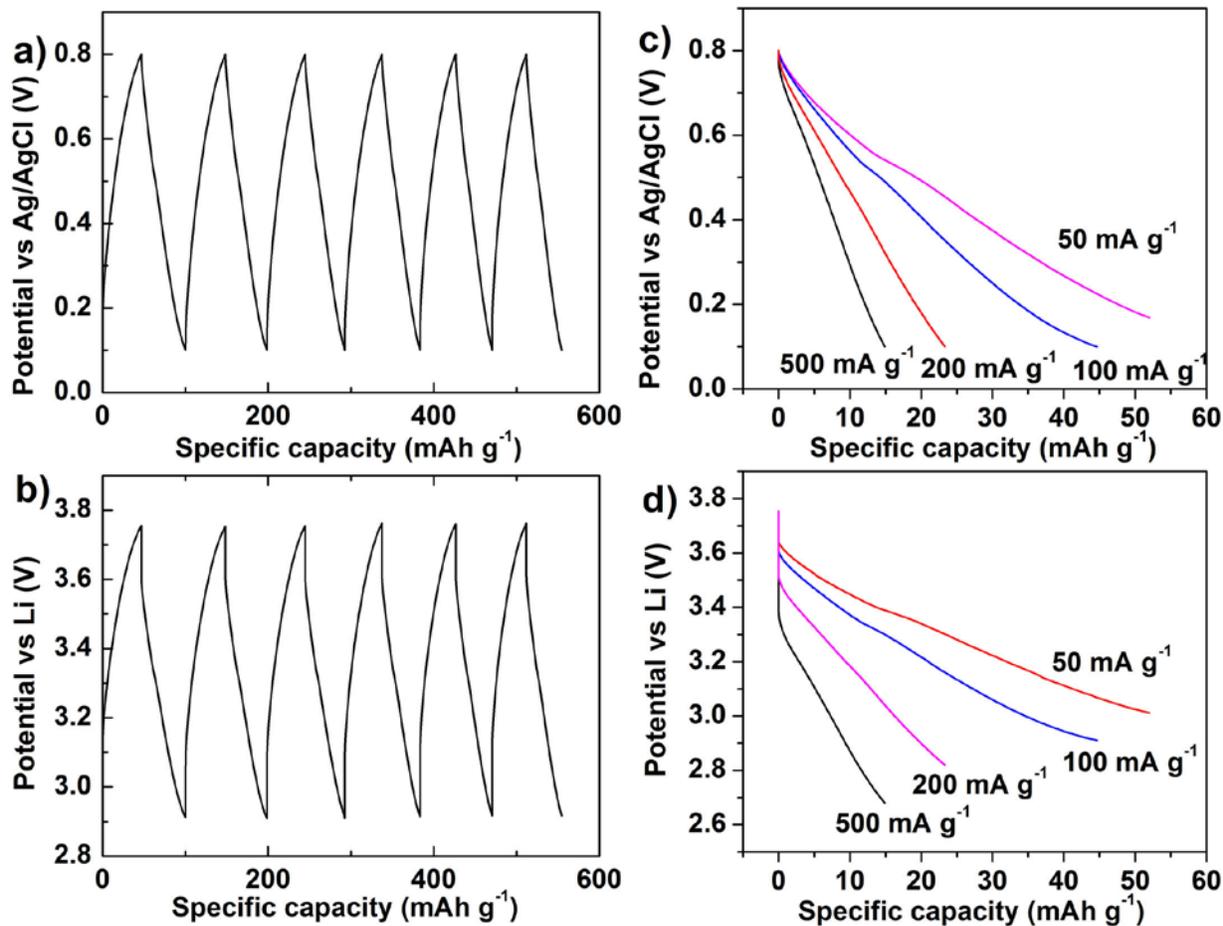


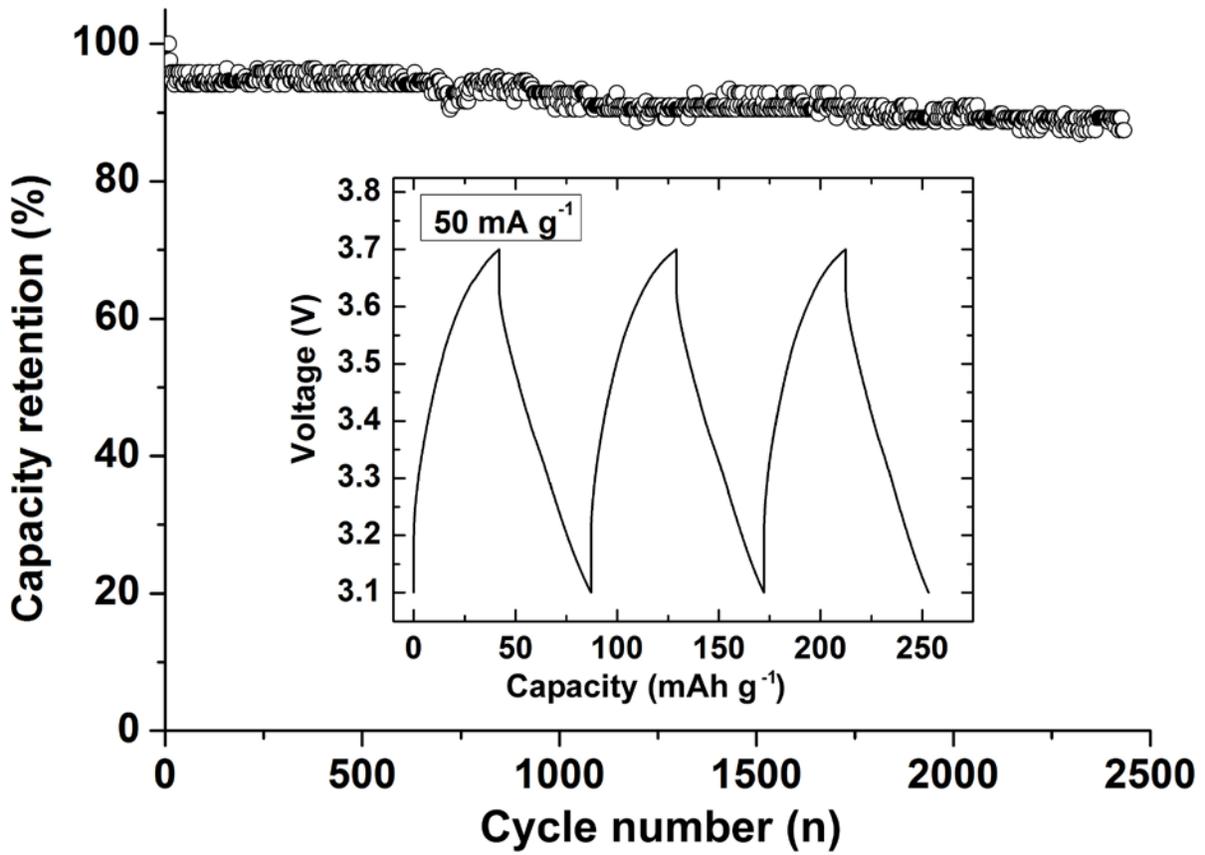
Figure 1. Schematic diagram of lithium-MnO<sub>2</sub> hybrid electrolyte system.



**Figure 2.** Cyclic voltammograms (CV) of Li hybrid electrolyte batteries at scan rate of  $1 \text{ mV s}^{-1}$  (a) and  $20 \text{ mV s}^{-1}$  (b) using Ag/AgCl as the reference electrode.



**Figure 3.** Charge and discharge curves at a rate of 50 mA g<sup>-1</sup> (a,b) and different rate discharge curves from 50 mA g<sup>-1</sup> to 500 mA g<sup>-1</sup> (c,d) for Li-MnO<sub>2</sub> hybrid electrolyte batteries versus Ag/AgCl reference electrode (a,c) and lithium electrode (b,d) using the three electrode system.



**Figure 4.** Cycle life of Li-MnO<sub>2</sub> hybrid electrolyte battery at a rate of 50 mA g<sup>-1</sup> using the 2-electrode system between 3.1 and 3.7 V. The inset shows the charge and discharge curves.