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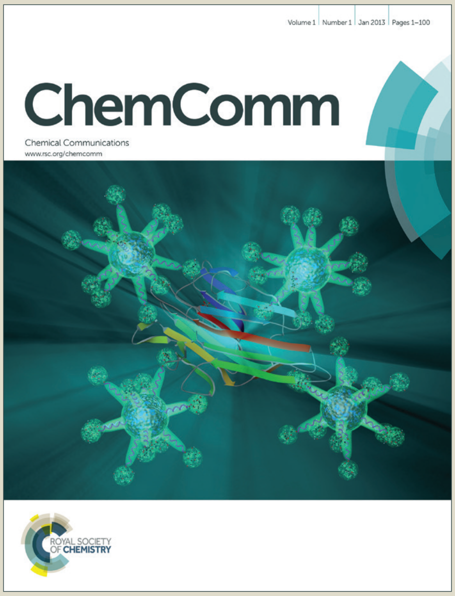

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An acid-free rechargeable battery based on $PbSO_4$ and spinel $LiMn_2O_4$

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An acid-free lead rechargeable battery system comprising $PbSO_4$ as the negative electrode, $LiMn_2O_4$ as the positive electrode and a neutral Li_2SO_4 aqueous solution as electrolyte is reported and its electrochemical performance is very good. It provides a great promise to reduce the global use of lead by 50% since its cost is also low.

Batteries are currently being further developed to power an increasingly diverse range of applications, from portable electronics, electric vehicles to smart grids.[1] The lead-acid battery is commercially one of the most successful electrochemical systems, and no other battery is yet able to replace it in the field of energy storage. Its market share is still increasing in the last years, albeit batteries based on other chemistries are rapidly catching up.[2,3] The main reasons for this are its specific advantages including low cost, high reliability, and easy construction. In addition, its raw materials are practically unlimited, about 95 % can be recycled. However, sulphuric acid, which is used as the electrolyte for lead acid battery, causes serious damage to equipment, and Pb leads to serious environmental pollution. As a result, it is urgently needed to reduce the used amount of lead and acid.

Recently, most research in this area has focused on electrodes and electrolytes of batteries.[4,5] For example a capacitor-battery system based on a PbO_2 positive electrode and activated carbon negative electrode was reported.[5] However, it still uses acid and the amount of Pb can only be reduced by 25 wt.% at most. In addition, its energy density is below 50 % of that of lead acid battery, lower than 25 Wh kg^{-1} although its rate capability and cycling life is much improved. In order to increase the specific capacity of lead batteries and reduce the amount of Pb and acid, here we reported an acid-free lead battery based on $PbSO_4$ as a negative electrode and spinel $LiMn_2O_4$ as a positive electrode in 0.5 M Li_2SO_4 neutral aqueous electrolyte. Its cycling performance is excellent with 100 % Coulombic efficiency and its energy density can be 68 Wh kg^{-1}.

The preparation of the spinel $LiMn_2O_4$ is as follows. At first, a nanowire birnessite-MnO_2 (δ-MnO_2) was synthesized by a hydrothermal reaction from a solution of $MnSO_4$, $(NH_4)_2S_2O_8$ and $(NH_4)_2SO_4$ in a molar ratio of 1: 1: 4 at 140 °C as we described previously.[3a] The prepared δ-MnO_2 nanowires were milled with $LiOH\cdot H_2O$ in ethanol; then the mixture was sonicated for 5 h. After the ethanol was evaporated, the mixture was transferred into a furnace and heat-treated at 700 °C for 8 h to get $LiMn_2O_4$ nanocubes.

The spinel $LiMn_2O_4$ nanocubes were analysed by X-ray diffraction on a Bruker D4 X-ray diffractometer with Ni-filtered CuK_α radiation. They were mixed with acetylene black and poly (tetrafluoroethylene) (PTFE) in a weight ratio of 7.5:1.5:1 dispersed in ethanol. After drying, the mixture was pressed into a film with an active mass loading of about 3.75 mg/cm^2, the film was cut into a disk of about 2 mg which was pressed onto Ni-grid at a pressure of 10 MPa, and finally dried at 120 °C for 12 h to act as the positive electrode. The cyclic voltammetric (CV) testing of $LiMn_2O_4$ electrodes was performed in 0.5 M Li_2SO_4 aqueous solution in a three-electrode cell with a nickel grid and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. The CV data were collected on an electrochemical working station of CHI660C (Chenhua, China).

$PbSO_4$ powder (>99.9 wt%) was purchased from Second Shanghai Smelting Plant (China) and used as received. The $PbSO_4$ electrode was prepared in the same way as the $LiMn_2O_4$ electrode. A two-electrode cell consisting of the above $LiMn_2O_4$ positive electrode and the $PbSO_4$ negative electrode with a distance of about 1 cm was used to test the charge-discharge and cycling behavior of the as-prepared $LiMn_2O_4$ in 0.5 M Li_2SO_4 solution on a Land 2001A cell tester.

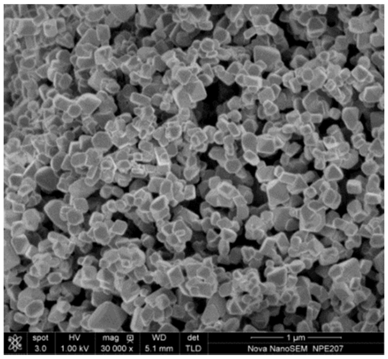


Fig. 1 Field emission scanning electron micrograph (FESEM) of the prepared $LiMn_2O_4$ nanocubes.

The X-ray diffraction pattern (Fig. S1, ESI†) shows that the as-prepared $LiMn_2O_4$ is highly crystalline with spinel structure; the characteristic peaks of planes can be clearly identified. This high degree of ordering is caused by the high temperature treatment (700 °C) during the synthesis process. FESEM micrograph of the prepared $LiMn_2O_4$ (Fig. 1) shows clearly that this material exists in nanocubes. This is different from the prepared Na_xMnO_2 nanorods from the heat-treatment of Na_2CO_3 with the MnO_2 nanowires.[3a] The main reason are presumably differences in the crystallization processes.

Cyclic voltammogramms (CVs) of $PbSO_4$ and $LiMn_2O_4$ electrodes in 0.5 M Li_2SO_4 aqueous electrolyte at the scan rate of 5 mV s^{-1} are shown in Fig. 2. In the case of $PbSO_4$, there is one set of redox peaks located at -0.6/-0.36 V (vs. SCE), which is due to the redox reaction of $PbSO_4$/Pb. This implies that $PbSO_4$ is stable in neutral aqueous solution and its redox reactions can reversibly take place. Two sets of redox peaks related to $LiMn_2O_4$ are situated at 0.62/0.86 V and 0.78/1.0 V (vs. SCE), respectively, which correspond to the intercalation/de-intercalation of Li^+ ions into/from $LiMn_2O_4$ in the aqueous electrolyte solution. This is similar to our former reports. [6] Since there is a potential difference between $PbSO_4$ and $LiMn_2O_4$, they can be assembled into a battery system whose redox reactions during charge/discharge processes can be schematically shown in Scheme 1.

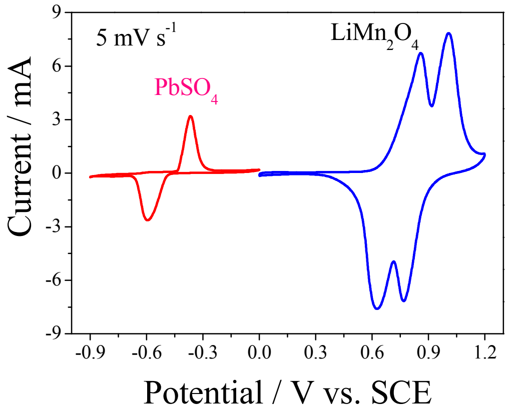
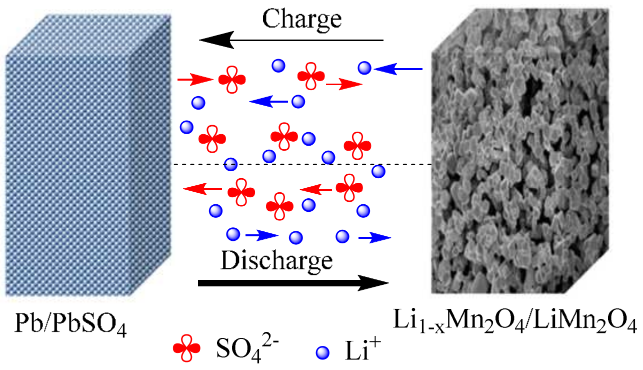


Fig. 2 Cyclic voltammogramms (CVs) of $PbSO_4$ and $LiMn_2O_4$ electrodes in 0.5 M Li_2SO_4 aqueous electrolyte at the scan rate of 5 mV s^{-1}, which was tested by using nickel-grid and SCE as the counter and reference electrodes, respectively, and each electrode is about 2 mg.



Scheme 1 Schematic illustration of the redox reactions for acid-free $PbSO_4$// $LiMn_2O_4$ aqueous rechargeable battery during the charge/discharge processes.

Their electrode and cell reactions are shown simplified as the following:

Negative electrode:

$$PbSO_4 + 2\,e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Pb + SO_4^{2-} \qquad (1)$$

Positive electrode:

$$LiMn_2O_4 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_{1-x}Mn_2O_4 + x\,Li^+ + x\,e^- \qquad (2)$$

Cell reaction:

$$x/_2\,PbSO_4 + LiMn_2O_4 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} x/_2\,Pb + Li_{1-x}Mn_2O_4 + x\,Li^+ + x/_2\,SO_4^{2-} \qquad (3)$$

During charging $PbSO_4$ is turned into Pb by releasing sulphate anions into the neutral aqueous electrolyte. In the meanwhile, $LiMn_2O_4$ is turned into $Li_{1-x}Mn_2O_4$ by releasing Li^+ cations into the electrolyte. As a result, the released sulphate anions and lithium cations keep the electrolyte always electrically neutral. During the discharge process, Pb gets SO_4^{2-} anion from the neutral electrolyte to turn into $PbSO_4$ together with the gain of Li^+ ion from the electrolyte into $Li_{1-x}Mn_2O_4$ to become $LiMn_2O_4$. This means that this battery does not need acid solution since the positive electrode is $LiMn_2O_4$ instead of PbO_2. The latter needs an acid media to realize its fast redox reaction to $PbSO_4$.

According to the definition of aqueous rechargeable lithium batteries (ARLBs),[7] it can be assigned as a 1st generation ARLBs type. During the charge or discharge process, both electrodes exist as solid phases, and the total volume change is less than those for Zn//$LiMn_2O_4$, Zn//$LiFePO_4$ or Zn//Na_xMnO_2 [3] since Pb or $PbSO_4$ could not dissolve into the neutral solution as Zn.

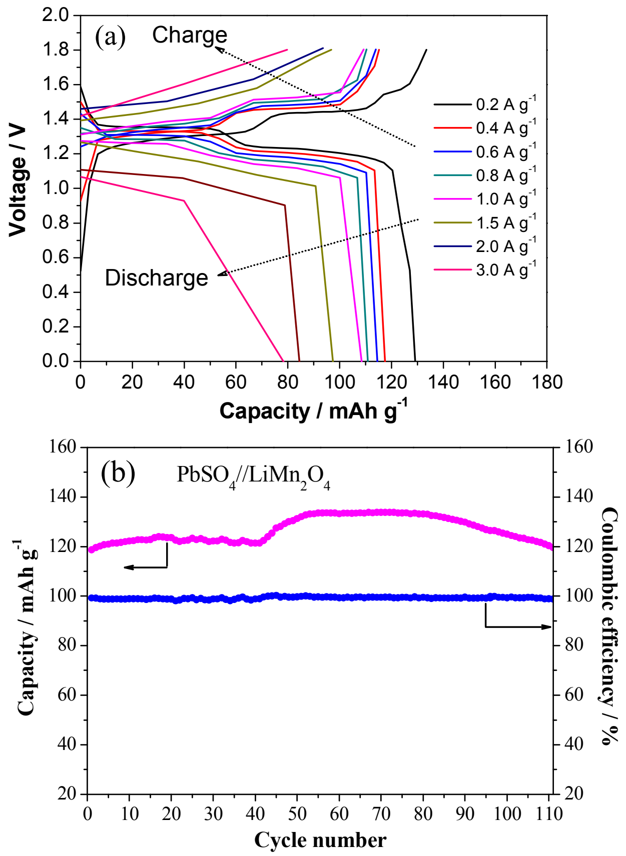


Fig. 3 (a) Charge and discharge curves of the $PbSO_4/Li_2SO_4/LiMn_2O_4$ battery at different current densities based on the spinel positive electrode, and (b) cycling performance of the battery at 400 mA g^{-1} based on $LiMn_2O_4$.

The electrochemical performance of the $PbSO_4$//$LiMn_2O_4$ battery at different current densities between 0-1.8 V is shown in Fig. 3. At the lower current densities two discharge/charge voltage platforms at about 1.27/1.35 V and 1.44/1.23 V, respectively, can be identified which are consistent with the CV results. This is due to the intercalation/deintercalation of Li^+ ions into/from different sites of the spinel host. Its average discharge voltage is 1.30 V. The reversible capacity of the battery is 128 mAh g^{-1} at 200 mA g^{-1} based on the $LiMn_2O_4$ positive electrode, which is similar to the reported value with aqueous electrolytes.[6] When the charge/discharge current increases from 0.4, 0.6, 0.8, 1.0, 1.5, 2.0 to 3.0 A g^{-1}, the discharge capacity decreases from 117.5, 114.6, 110.9, 108.8, 97.5, 94.6, to 78.4 mAh g^{-1}, respectively. This suggests that the acid-free lead battery can be charged and discharged fast, and can meet the rapid change of power supply and demand from the grid (Fig. S2, ESI†). However, its rate capability cannot be compared with those of $LiNi_{0.5}Mn_{1.5}O_4$ and $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$,[8] The main reason is the slow redox kinetics of $Pd/PbSO_4$, this is also a key problem for the lead acid rechargeable batteries.[9]

In the case of the lead acid battery, about half of the theoretical capacity of the negative electrode can be obtained practically. Applying this to the present battery system the practical capacity of $PbSO_4$ would be about 88 mAh g^{-1}. Combining the practical capacity of $LiMn_2O_4$ (128 mAh g-1) and the average discharge voltage (1.3 V), the calculated energy density based on the two electrodes will be 68 Wh kg^{-1}. This value is comparable with that of lead acid batteries.

The cycling performance of the $PbSO_4//LiMn_2O_4$ at the full discharge capacity of 128 mAh g^{-1} based on $LiMn_2O_4$ at the current density of 400 mA g^{-1} (Fig. 3b) shows that the Coulombic efficiency is almost 100 % except in the initial cycles, this again is similar to lithium ion batteries. This means that the acid-free lead battery shows good charge and discharge reversibility. In terms of the spinel $LiMn_2O_4$, it is very stable, its redox potential is below that of oxygen evolution and it can be cycled up to 10 000 full cycles.[6] For the redox couple $Pb/PbSO_4$, Fig. 2 shows clearly that its redox potential is above that for hydrogen evolution due to the large hydrogen overpotential of Pb. In the case of $LiMn_2O_4$, its redox potentials are also below that of oxygen evolution, which has been well illustrated in ARLBs.[1d],[6a,6b,7] As a result, there are basically no side reactions (gassing) resulting in 100 % Coulombic efficiency which is evidently higher than that of lead acid battery. Another reason is that the charge cut-off voltage is 1.8 V, much lower than 2.4 V for lead acid battery. If it is used for energy storage, this means that it is superior to lead acid battery since its self-discharge rate will also be lower due to lower working voltage and less irreversible reactions. After 110 full cycles, the capacity loss based on $LiMn_2O_4$ is less than 1 % compared with the initial cycles. In the case of the $Pb/PbSO_4$ electrode, it is known that there is no phase change and dendrite problem like Zn, it will be stable during cycling. As a result, the cycling behavior of this battery system will be superior to the reported $Zn//LiMn_2O_4$ and $Zn//Na_xMnO_2$,[3] which can be above 1000 cycles. Of course, further research on the extended cycling is needed.

In conclusion, an acid-free lead battery has been assembled using $PbSO_4$ as the negative electrode, spinel $LiMn_2O_4$ nanocubes as the positive electrode, and an aqueous solution of 0.5 M Li_2SO_4 as the electrolyte. Its average discharge voltage is 1.3 V and the specific capacity based on the spinel is stable at 128 mAh g^{-1}. The calculated energy density based on the practical capacities of the two electrodes is 68 Wh kg^{-1}. The battery system shows less than 1 % capacity loss after 110 full cycles at the current density of 400 mA g^{-1} between 0-1.8 V and 100% Coulombic efficiency except the initial several cycles. The above results show clearly that the positive electrode of lead acid battery (PbO_2) can be completely substituted by the environmentally friendly and cheap $LiMn_2O_4$, which means that 50 % of Pb can be saved. In addition, sulphuric acid is not needed. It will be more friendly to the operators and during use. Our battery system can be a good candidate as a power source for electric bicycles or energy storage on a large scale.

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Notes and references

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Electronic Supplementary Information (ESI) available: X-ray diffraction pattern of the as-prepared $LiMn_2O_4$ and change of capacity of the battery at different current densities. See DOI: 10.1039/c000000x/

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Table of Content

An acid-free rechargeable battery based on $PbSO_4$ and spinel $LiMn_2O_4$

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A low cost and better friendly rechargeable battery with good electrochemical performance, which is of great promise to reduce the use amount of Pb by 50%.