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A lithium ion battery using an aqueous electrolyte solution

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Energy and environmental pollution have become the two major problems in today's society. The development of green energy storage devices with good safety, high reliability, high energy density and low cost are urgently demanded. Here we report on a lithium ion battery using an aqueous electrolyte solution. It is built up by using graphite coated with gel polymer membrane and LISICON as the negative electrode, and LiFePO₄ in aqueous solution as the positive electrode. Its average discharge voltage is up to 3.1V and energy density based on the two electrode materials is 258Wh kg⁻¹. It will be a promising energy storage system with good safety and efficient cooling effects.

Recently, the rapid depletion of fossil fuels and the increasing emission of greenhouse gases causing air pollution have become serious issues. Development of the next generation of green energy storage devices is urgently demanded^{1–3}. New energy industry including electric vehicles and large-scale energy storage systems (ESSs) such as smart grids requires energy storage systems with good safety, high reliability, high energy density and low cost. Hence, “three E” criteria, namely, energy (high energy densities with respect to unit weight and volume), economics (low manufacturing costs and long cycling life), and environment (safe, non-toxic and high reliability) is used to determine the suitable ESS that meets the needs of application^{4–6}. Although lithium ion batteries (LIBs) show good promise with some quite dominant advantages over conventional batteries, their applications in large-scale ESS such as electric vehicles and smart grids are still not commercially viable due to their inherent safety problems related to the use of high cost, toxic and flammable organic electrolyte and slow charging performance^{7–9}.

Since aqueous rechargeable lithium batteries (ARLBs) using positive electrode materials from commercial LIBs were first introduced in 1994, they have attracted wide attention as a promising system because of their low capital investment, environmental friendliness and good safety^{10–12}. Additionally, the organic electrolyte solution is replaced by the non-flammable aqueous electrolyte with high ionic conductivity, about 2 orders of magnitude higher than those of the organic electrolytes, which can lead to good rate performance and low over potentials. Recent results show that nanostructured materials as positive electrode materials for ARLBs present much better electrochemical performance than LIBs using organic electrolytes. For example, LiMn₂O₄ nanotube shows a superfast second-level charge and discharge capability and excellent cycling behavior because of the nanostructure and preferred orientation^{13–15}. Recently, we prepared a coated lithium metal, which is stable in aqueous electrolytes, to build an ARLB with a stable working voltage of 4.0 V, a break-through the window of electrochemical stability of water (1.229 V) has been achieved^{16–20}. They can be a suitable alternative because their energy density can be above that of the corresponding lithium ion batteries. However, the use of Li metal as the negative electrode in conventional lithium metal secondary batteries are restricted by cycling due to dendrites, which can break down during the cycling and lead to sudden death of the battery. Recently, another kind of ARLB, aqueous lithium ion battery, was reported with stable voltage up to 3.0 V due to the use of ‘water-in-salt’ electrolyte²¹.

Here, we report another aqueous lithium ion battery (ALIB) which consists of graphite instead of Li metal as the negative electrode, which presents excellent cycling, and commercial LiFePO₄ as the positive electrode in aqueous electrolyte. Its capacity is up to 121 mAh g⁻¹ on the basis of LiFePO₄ with excellent cycling performance and satisfactory rate capability.

Results

As shown in Fig. S1 of ESI (electronic supporting information), the coated graphite acted as the negative electrode. Graphite on the copper current collector was at first coated with a gel polymer electrolyte (GPE), which was

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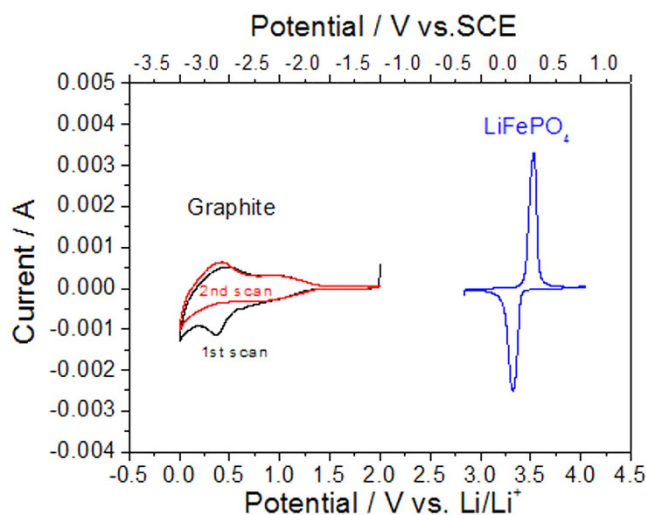


Figure 1. CVs for graphite negative electrode in 1 mol l^{-1} LiClO_4 solution with ethylene carbonate, diethyl carbonate and dimethyl carbonate (volumetric ratio 1:1:1) and LiFePO_4 positive electrode in 0.5 mol l^{-1} Li_2SO_4 aqueous solution by using Ni mesh and saturated calomel electrode (SCE) as the counter and the reference electrodes, respectively, at the scan rate of 0.5 mV s^{-1} .

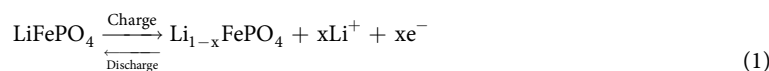
made by a composite polymer membrane PVDF (poly(vinylidene fluoride)) with NWFs (nonwoven fabrics)²² of $40 \mu\text{m}$ saturating with the 1 mol l^{-1} LiClO_4 solution in ethylene carbonate, diethyl carbonate and dimethyl carbonate (volumetric ratio is 1:1:1). Its ionic conductivity of Li^+ ions is about 0.3 mS cm^{-1} at room temperature. Then, a LISICON film consisting of $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5\text{-TiO}_2\text{-GeO}_2$, which was bought from Ohara Inc., Japan, was further simply put on the GPE. Thickness and ionic conductivity of the LISICON film are $150 \mu\text{m}$ and 0.1 mS cm^{-1} at room temperature, respectively. If LISICON film contacts Li metal or lithiated graphite directly, some metal oxides such as GeO_2 in the LISICON film will be reduced by Li metal leading to poor ionic conductivity. As a result, the GPE ensures the good electrochemical stability of the LISICON film. Here, the LISICON film acted as a solid separator to keep water away and allowed only the passage of Li^+ ions. Then a passage of Li^+ ions between the coated graphite negative electrode and the aqueous solution was built up.

The cyclic voltammograms (CVs) of the graphite negative electrode in 1 mol l^{-1} LiClO_4 solution and that of LiFePO_4 in 0.5 mol l^{-1} Li_2SO_4 aqueous solution at the scan rate of 0.5 mV s^{-1} are shown in Fig. 1. In the case of graphite, there is a reduction peak at 0.4 V (vs. Li/Li^+) in the first scan corresponding to the formation of SEI (solid electrolyte interface). Next, the reversible Li^+ ion intercalation-deintercalation process occurred at about 0.2 V (vs. Li/Li^+). In the second scan, there is only one pair of redox peaks for Li^+ ion intercalation-deintercalation. The charge and discharge curves of graphite in the 1st, 2nd 4th and its cycling performance are shown in Fig. S2a. Similar to former reports, there is some slight irreversible capacity in the first cycle due to the formation of SEI film. However, from the second cycle, the capacity is stable and the coulomb efficiency can be about 100% with a reversible capacity of around 120 mAh g^{-1} . These results are consistent with the above CV results.

Commercial LiFePO_4 (see Fig. S3 for morphology and X-ray diffraction in ESI) is a positive electrode material for lithium-ion batteries with good thermal stability and environmental benign²³. Its main redox peaks for the deintercalation/intercalation of Li^+ ions in 0.5 mol l^{-1} Li_2SO_4 aqueous solution are located at 0.3 V and 0.1 V (vs. SCE), respectively, which is consistent with the formerly reported intercalation/deintercalation behavior of LiFePO_4 in the aqueous electrolytes²³. The separation of the redox peaks is much narrower than that in the organic electrolyte²⁴.

Based on the above discussion, both the coated graphite and LiFePO_4 in aqueous electrolyte provide reversible Li^+ intercalation and deintercalation. They establish another ALIB whose electrode reactions is shown in the following equations (1–3):

Positive electrode reaction:



Negative electrode reaction:



Total reaction:

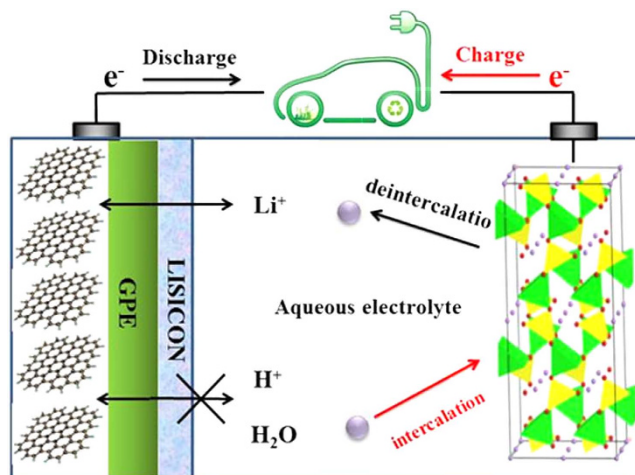
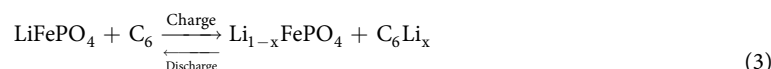


Figure 2. Schematic illustration of our designed ALIB using the graphite coated by GPE and LISICON as negative electrode, LiFePO_4 in $0.5 \text{ mol l}^{-1} \text{ Li}_2\text{SO}_4$ aqueous electrolyte as positive electrode.



wherein $x \leq 1$. During the charge process, Li^+ ions deintercalate from the LiFePO_4 olive structure and electrons flow via the outer circuit. The deintercalated Li^+ ions pass through the aqueous solutions, LISICON film and GPE, and intercalate in the graphite through reduction by electrons from the outer circuit. During the discharge process, the reverse process takes place. The resulting scheme is shown in Fig. 2. Since its positive electrode is put into aqueous electrolyte solution instead of an organic one, it is called an aqueous lithium ion battery (ALIB).

The CV curve of the ALIB at the scan rate of 0.1 mV s^{-1} in Fig. S4 also shows a couple of redox peaks situated at 3.43 and 3.15 V, respectively, indicating the good reversibility. Here the Li^+ intercalation-deintercalation potential of graphite is much lower than that for hydrogen evolution. The reversible intercalation-deintercalation process will not happen in water. However, in our case, Li^+ ions act as the charge transfer media, which can cross over the hydrogen evolution potential through LISICON and arrive at the graphite negative electrode directly. This cross-over is similar to the potential change between both sides of a cell membrane, the potential of Li^+ ions decrease very sharply from the positive electrode to the negative one¹⁶. The Li^+ ions in the positive side have higher potential and are very stable. Meanwhile, water and protons could not enter into the negative side with a low potential so that hydrogen could not be produced. As to the LiFePO_4 positive electrode, it is stable in water since its potential is below that for the oxygen evolution and much higher than that for hydrogen evolution¹⁸.

The electrochemical performance of the assembled ALIB is shown in Fig. 3. In the first cycle between 2.5 and 4.2 V at 100 mA g^{-1} based on the positive electrode (Fig. 3a), there are two distinct voltage plateaus at 3.39 and 3.11 V, respectively, which are in good agreement with the above CV results. At 100 mA g^{-1} the initial charge and discharge capacities of this battery based on the mass of LiFePO_4 are 149 and 121 mAh g^{-1} (Fig. 3b), respectively, and the initial coulomb efficiency is 81.2%. Its discharge capacities can be comparable to those of LiFePO_4 as positive electrode in aqueous or organic electrolytes. The charge and discharge curves in the 10th and the 20th cycles for the assembled ALIB overlap very well, indicating a good reversibility. The energy density of this ALIB is 258 Wh kg^{-1} based on the cell voltage and cell capacity, which is much higher than those of previously reported ARLBs ($30\text{--}45 \text{ Wh kg}^{-1}$), whose voltages are below 2 V ¹⁴, and that of ALIB ($<120 \text{ Wh kg}^{-1}$)²¹. If graphite with higher capacity is used, the energy density will be higher.

The assembled ALIB presents 95.8% capacity retention at the current density of 50 mA g^{-1} based on the mass of LiFePO_4 after 24 cycles. When the rate increases, the capacity retention of this ALIB is still very good (Fig. 3c). For example, at a rate of 0.5C, 1C, 2C, 3C, 5C, the discharge capacities based on the mass of LiFePO_4 are 131, 118, 100, 95 and 80 mAh g^{-1} , respectively. Though it is poorer than that of the first generation ARLBs, it is comparable with those of LIBs.

Discussion

Our design is different from our previous work and conventional lithium ion battery though both sides are based on the traditional intercalation/deintercalation reactions. On the one hand, we do not use the coated Li metal as the negative electrode due to the problem of its lacking stability. On the other hand, the aqueous electrolyte has higher thermal capacitance and can absorb large amounts of heat. During the same charge-discharge process, the temperature of this system will be more stable in comparison with that of the conventional lithium ion batteries. Water or aqueous electrolyte is in direct contact with both the negative and the positive electrodes, and the cooling effects are very efficient. A cooling system, which is usually required for large capacity battery modules, is not needed for the application of this battery in electric vehicles. If other intercalation compounds such as LiMn_2O_4 , LiCoO_2 and $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, which are stable in aqueous electrolytes, are used as the positive

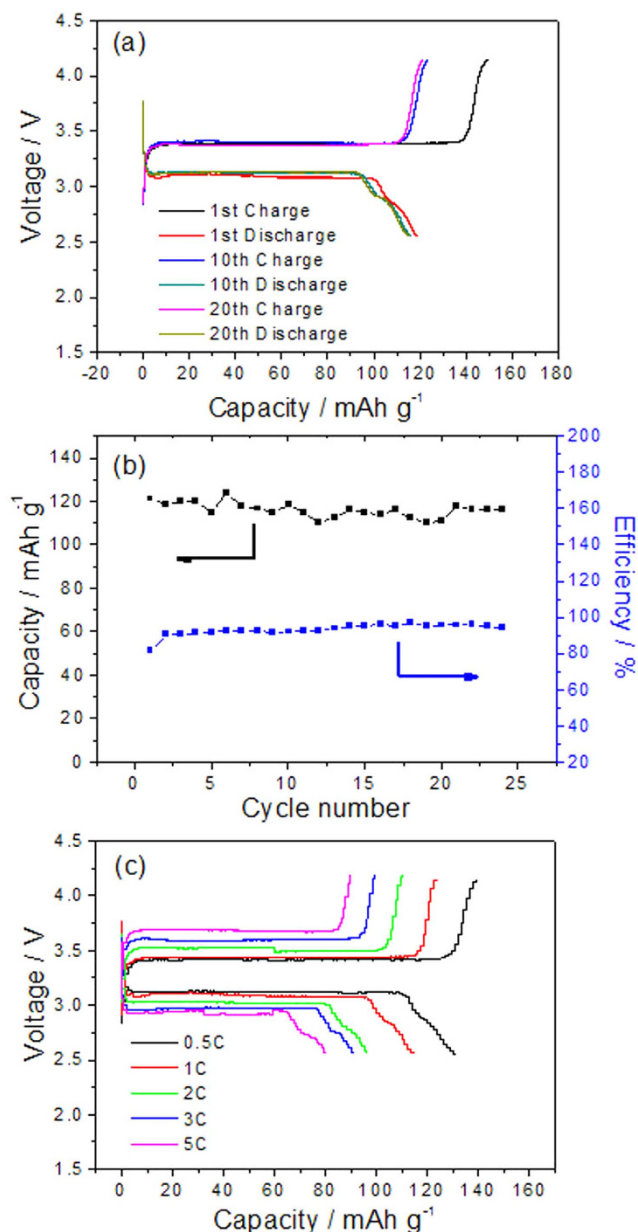


Figure 3. Electrochemical performance of the assembled ALIB: (a) Galvanostatic charge-discharge curves in the first, 10th, 20th cycles at the current density of 100 mA g^{-1} based on the positive electrode between 2.5 and 4.2 V, (b) the cycling performance between 2.5 and 4.1 V at the current density of 100 mA g^{-1} based on the LiFePO_4 positive electrode, and (c) charge-discharge curves at different rates.

electrode^{25–27}, not only the average discharge voltage will be higher but also the energy density and cycling performance will be improved. In addition, here the composite polymer membrane is flame retarding and becomes a gel after saturating with the organic electrolyte, which presents much slower evaporation speed in comparison with the organic electrolytes²⁴. This design is also different from the reported ALIB whose stable voltage is up to 3.0 V due to the large polarization or overpotentials due to the use of ‘water-in-salt’ electrolyte²¹. As a result, it will be a promising energy storage system.

However, there are some problems related to the possible practical applications by adopting the solid state electrolytes (LISICON) due to the following two reasons. (1) Its cost is high, and future methods to decrease its manufacturing cost are needed since its primary materials are not expensive; its ionic conductivity at room temperature is not high enough so that large over potential or polarization is produced. It is encouraging that many endeavours are under way^{20,28}.

In summary, our work provides another aqueous lithium ion battery (ALIB) using graphite coated with GPE and LISICON as the negative electrode, lithium intercalation compound LiFePO_4 in $0.5 \text{ mol l}^{-1} \text{ Li}_2\text{SO}_4$ aqueous solution as the positive electrode. It is much safer than the traditional lithium ion batteries since water or aqueous electrolyte solution provides efficient cooling effects. Its average discharge voltage is 3.1 V, much higher than the

window of electrochemical stability of water (1.229 V). Based on the mass of both electrodes, its energy density can be 258 Wh kg⁻¹, and the cycling behaviour is satisfactory.

Method

Coated graphite electrode. The graphite electrode was prepared by coating the N-methyl-2-pyrrolidone (NMP)-based slurry containing the commercial graphite, acetylene black and poly(vinylidene difluoride) (PVDF) in a weight ratio of 8:1:1 on copper foil (thickness: 20 μm) using a doctor-blade technique. The coated foils were dried and punched into circular pieces (d = 15 mm), which were further dried at 120 °C for 12 h under vacuum. The mass loading of graphite was about 25 mg cm⁻². The graphite electrode was at first simply coated (like casing) by a home-made gel polymer electrolyte (GPE), whose ionic conductivity is about 0.2 mS cm⁻¹ at room temperature. The GPE was made by saturating a composite polymer membrane, PVDF (poly(vinyl difluoride)) with nonwoven fabric²², with a thickness of 40 μm with the 1 mol l⁻¹ LiClO₄ solution in ethylene carbonate, diethyl carbonate and dimethyl carbonate (volumetric ratio is 1:1:1)²³. Then, a LISICON film consisting of Li₂O-Al₂O₃-SiO₂-P₂O₅-TiO₂-GeO₂, which was bought from Ohara Inc., Japan, was further simply put on the GPE. Thickness and ionic conductivity of the LISICON film are 150 μm and 0.1 mS cm⁻¹ at room temperature, respectively.

Assembling of aqueous lithium ion battery (ALIB). The commercial LiFePO₄ was mixed with acetylene black and poly(tetrafluoroethylene) (PTFE) in a weight ratio of 8:1:1 with the help of ethanol. After drying, the mixture was pressed into a film with an active mass loading of 3.75 mg cm⁻², then the film was cut into disks. These disks were pressed onto Ni-grid at a pressure of 10 MPa and dried at 80 °C for one night. The coated graphite and LiFePO₄ were immersed into the 0.5 M Li₂SO₄ aqueous solution to make up an aqueous lithium ion battery.

Characterization and electrochemical testing. X-ray powder diffraction (XRD) was carried out using a Bruker Analytical X-ray System with Cu Kα radiation source filtered by a thin nickel plate. Scanning electron micrographs (SEM) were obtained with a Philips XL30 scanning electron microscope. Cyclic voltammetry (CV) and galvanostatic charging/discharging were performed at room temperature on an electrochemical working station CHI600C (Chenhua, Shanghai, China) and a cell tester 2001A (Land, Wuhan, China), respectively.

References

- Dunn, B., Kamath, H. & Tarascon, J. M. Electrical energy storage for the grid: a battery of choices. *Science*, **334**, 928–935 (2011).
- Chen, X., Li, C., Grätzel, M., Kostecki, R. & Mao, S. S. Nanomaterials for renewable energy production and storage. *Chem. Soc. Rev.* **41**, 7909–7937 (2012).
- Chang, Z., Yang, Y. Q., Li, M. X., Wang, X. W. & Wu, Y. P. Green energy storage chemistries based on neutral aqueous electrolytes. *J. Mater. Chem. A* **2**, 10739–10755 (2014).
- Liu, J. Addressing the Grand Challenges in Energy Storage. *Adv. Funct. Mater.* **23**, 924–928 (2013).
- Kim, T. H. *et al.* The Current Move of Lithium Ion Batteries Towards the Next Phase. *Adv. Energy Mater.* **2**, 860–872 (2012).
- Yang, Z. G. *et al.* Electrochemical Energy Storage for Green Grid. *Chem. Rev.* **111**, 3577–3613 (2011).
- Tarascon, J. M. & Armand, M. Issues and challenges facing rechargeable lithium batteries. *Nature* **414**, 359–367 (2001).
- Wu, Y. P. *Lithium-ion batteries: Fundamentals and Applications*. CRC Press, New York, 2015.
- Goodenough, J. B. & Park, K. S. The Li-ion rechargeable battery: a perspective. *J. Am. Chem. Soc.* **135**, 1167–1176 (2013).
- Wu, L., Dahn, J. R. & Wainwright, D. S. Rechargeable lithium batteries with aqueous electrolytes. *Science* **264**, 1115–1117 (1994).
- Tang, W. *et al.* Aqueous rechargeable lithium batteries as an energy storage system of superfast charging. *Energy Environ. Sci.* **6**, 2093–2104 (2013).
- Alias, N. & Mohamad, A. A. Advances of aqueous rechargeable lithium-ion battery: A review. *J. Power Sources* **274**, 237–251 (2015).
- Qu, Q. T. *et al.* Porous LiMn₂O₄ as positive electrode material with high power and excellent cycling for aqueous rechargeable lithium batteries. *Energy Environ. Sci.* **4**, 3985–3990 (2011).
- Tang, W. *et al.* LiMn₂O₄ Nanotube as positive electrode material of second-level charge capability for aqueous rechargeable batteries. *Nano Lett.* **13**, 2036–2040 (2013).
- Liu, L., Tian, F. H., Zhou, M., Guo, H. P. & Wang, X. Y. Aqueous rechargeable lithium battery based on polyaniline and LiMn₂O₄ with good cycling performance. *Electrochim. Acta* **70**, 360–364 (2012).
- Wang, X. J., Hou, Y. Y., Zhu, Y. S., Wu, Y. P. & Holze, R. An aqueous rechargeable lithium battery using coated Li metal as negative electrode. *Sci. Rep.* **3**, 1401 (2013).
- Wang, X. J., Qu, Q. T., Hou, Y. Y., Wang, F. X. & Wu, Y. P. An aqueous rechargeable lithium battery of high energy density based on coated Li metal and LiCoO₂. *Chem. Commun.* **49**, 6179–6181 (2013).
- Hou, Y. Y. *et al.* Macroporous LiFePO₄ as a positive electrode for an aqueous rechargeable lithium battery of high energy density. *J. Mater. Chem. A* **1**, 14713–14718 (2013).
- Chang, Z. *et al.* Rechargeable Li/Br battery: a promising platform for post lithium ion batteries. *J. Mater. Chem. A* **2**, 19444–19450 (2014).
- Chang, Z. *et al.* Hybrid system for rechargeable magnesium battery with high energy density. *Sci. Rep.* **5**, 11931 (2015).
- Suo, L. M. *et al.* “Water-in-salt” electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* **350**, 938–943 (2015).
- Zhu, Y. S. *et al.* Composite of a nonwoven fabric with poly(vinylidene fluoride) as a gel membrane of high safety for lithium ion battery. *Energy Environ. Sci.* **6**, 618–624 (2013).
- Zhao, Y., Peng, L. L., Liu, B. R. & Yu, G. H. Single-crystalline LiFePO₄ nanosheets for high-rate Li-ion batteries. *Nano Lett.* **14**, 2849–2853 (2014).
- Zheng, J. X. *et al.* Janus solid-liquid interface enabling ultrahigh charging and discharging rate for advanced lithium-ion Batteries. *Nano Lett.* **15**, 6102–6109 (2015).
- Wang, G. J. *et al.* An aqueous rechargeable lithium battery with good cycling performance. *Angew Chem. Int. Ed.* **46**, 295–301 (2007).
- Qu, Q. T. *et al.* Porous LiMn₂O₄ as positive electrode material with high power and excellent cycling for aqueous rechargeable lithium batteries. *Energy Environ. Sci.* **4**, 3985–3990 (2011).
- Wang, F. X., Xiao, S. Y., Chang, Z., Yang, Y. Q. & Wu, Y. P. Nanoporous LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ as an ultra-fast charge positive electrode material for aqueous rechargeable lithium batteries. *Chem. Commun.* **49**, 9209–9211 (2013).
- Wang, Y., He, P. & Zhou, H. Li-redox flow batteries based on hybrid electrolytes: at The cross road between Li-ion and redox flow batteries. *Adv. Energy Mater.* **2**, 770–779 (2012).

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Author Contributions

Z.C. and C.L., designed this hybrid battery. Z.C., C.L. and Y.W. carried out the electrochemical experiments and other analysis. Z.C., C.L., B.C. and Y.W. analyzed and discussed the results and wrote the manuscript. Y.W., Y.Z., L.F., L.Z. and W.H. supervised the research project.

Additional Information

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