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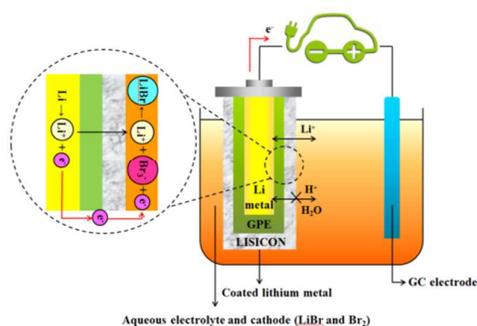
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Rechargeable Li//Br battery: A promising platform for post lithium ion batteries

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Li//Br battery, by using aqueous bromide/tribromide redox pair as positive electrode and a coated lithium metal as negative electrode, exhibit high energy density and good cycling.



ARTICLE

Rechargeable Li//Br battery: A promising platform for post lithium ion batteries

Cite this: DOI: 10.1039/x0xx00000x

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Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Another rechargeable lithium battery, Li//Br, is reported by using aqueous bromide/tribromide redox pair and a coated lithium metal as the positive and negative electrodes, respectively. The positive Br₂ electrode shows fast redox kinetic and good stability. This battery presents excellent electrochemical performance with an average discharge voltage up to 3.96 V at 1.7 mA cm⁻², an energy density of 1220 Wh kg⁻¹, a power density of 29.7 mW cm⁻² at current density of 12.8 mA cm⁻², and long cycling life. There is no evident voltage decrease after 100 cycles at 35% DOD. It would become a good platform between lithium ion batteries and Li//air batteries since the former shows lower energy density and the latter has quite some challenging problems to solve prior to practical application. This finding presents another promising choice for electrochemical energy storage systems.

1. Introduction

For the further development of electric vehicles which can reduce air pollution and global warming, battery systems with higher energy densities are urgently needed since the energy densities of current rechargeable batteries such as lithium ion batteries are too low to achieve enough driving distance¹⁻⁵. In 2008, it was released by the New Energy and Industrial Technology Development Organization (NEDO) in Japan that the energy density for a rechargeable battery should be above 500 Wh kg⁻¹ in the long term^{6,7}. Recently, Li//air or oxygen battery became a hot research topic since its theoretical energy density can be above 10000 Wh kg⁻¹ based on the Li metal and oxygen⁸. However, so far it has been well acknowledged that there are quite a lot of challenging scientific problems to solve prior to its practical application in the future^{9,10}. As a result, other rechargeable batteries such as Li//Se, Li//S and room temperature Na//S should be explored.¹¹

Aqueous rechargeable lithium batteries (ARLBs), which were invented in 1994 and attracted wide attentions again after 2007 as a promising system because of their low capital investment, environmentally friendly and good safety, can be an alternative since their energy densities can be above that of lithium ion batteries¹²⁻¹⁶. Additionally, the aqueous electrolyte is non-flammable and has high ionic conductivity, about 2 orders of magnitudes higher than those of the organic electrolytes, which can lead to good rate performance and low overpotentials^{17,18}. Several materials such as lithium intercalation compounds¹⁹, NiOOH²⁰, Cu²¹, oxygen^{10a}, I₃/I⁻²² and Fe(CN₆)₃⁻/Fe(CN₆)₄⁻ based aqueous electrolyte¹⁶ were

explored as positive electrodes. However, their electrochemical performance is still far from satisfaction.

A promising positive electrode in aqueous electrolyte should have the following characteristics such as high stability or solubility in water, proper redox potential avoiding the evolution of oxygen, and good reversibility without side reactions¹⁶. Thus, searching for alternative redox compounds is a direction of high priority. It is known that the tribromide/bromide (Br₃⁻/Br⁻) has a stable redox potential (1.05 V vs. SHE)²³ avoiding oxygen evolution and some solubility in water. This redox pair has a rapid electrochemical reaction with good reversibility as a charge carrier, for example, in dye-sensitized solar cells (DSSCs)²⁴, hydrogen//bromine fuel cell²⁵, Zn//Br₂ redox flow batteries (ZBB)²⁶ and alkali ion batteries²⁷. Here we report another lithium//bromine (Li//Br) battery²⁸ by using our former coated lithium metal as negative electrode^{13,19}, and the redox couple of Br₃⁻/Br⁻ as the positive electrode. Primary results show that this battery is of great promise due to high output voltage (3.96 V), high energy density (1220 Wh/kg⁻¹) and good cycling life.

2. Experimental

Assembly of aqueous Li//Br battery: The assembly of the negative electrode was conducted in an Ar-filled glove box (< 0.1 ppm H₂O and O₂). Li metal (spheric shape: 15 mm of diameter, and 0.5 mm of thickness) attached to a copper (Cu) mesh was simply coated (like casing) by a home-made gel polymer electrolyte (GPE), whose ionic conductivity is about 0.2 mS cm⁻² at room temperature. The GPE was made by saturating a sandwiched polymer membrane, PVDF

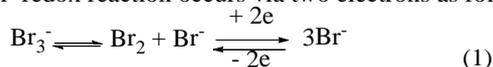
(poly(vinylidene fluoride)) /GFM (glass fiber mat)/PVDF, of 50 μm with a 1 mol L⁻¹ LiClO₄ solution in ethylene carbonate, diethyl carbonate and dimethyl carbonate (volumetric ratio is 1:1:1)²⁹. Then another layer of LISICON film was coated on the GPE layer. The films consisting of Li₂O-Al₂O₃-SiO₂-P₂O₅-TiO₂-GeO₂ was bought from Ohara Inc., Japan. Thickness and ionic conductivity of the LISICON film are 100 μm and 0.1 mS cm⁻² at room temperature, respectively. The specific area of the coated Li metal to contact the aqueous electrolyte is about 0.15 cm². The positive electrode comprised of an aqueous solution of Br₂, and LiBr (Sinopharm Chemical Regent Co., Ltd) solution was used as the electrolyte with a pH of 5.6, which can neglect the oxidation of Br⁻ into BrO⁻. Glass carbon, which has 0.07 cm² (0.3 cm diameter) geometric area, was used as the current collector for the positive electrode.

Electrochemical measurements: The electrochemical reactions were investigated by using cyclic voltammetry (CV) and galvanostatic charge/discharge test at room temperature. CV was performed at different scan rate for Br₂ single electrode by using an electrochemical workstation (CHI660C, Shanghai). The electrochemical window of the glassy carbon was tested in an aqueous Li₂SO₄ solution (0.5 mol L⁻¹) by a three-electrode cell where platinum and saturated calomel electrode (SCE, 0.242 V vs. SHE: standard hydrogen electrode) were used as the counter and reference electrodes, respectively. For the Li//Br battery, its battery performance was tested by using a two-electrode cell. The galvanostatic charge-discharge tests for the total battery at different deep of discharge were carried out by using a Land cyler (Wuhan, China). The specific energy density was calculated from the mass of active substance of Li, Br₂ and the average discharge voltage.

3. Results and discussion

Electrochemical performance of bromine single electrode

The Br₃⁻/Br⁻ redox reaction occurs via two electrons as follows:



Aqueous solution of LiBr shows higher ionic conductivity (see Supplementary Fig. S1), which can be up to 197.3 mS cm⁻¹ at room temperature at 7 mol L⁻¹, than aqueous electrolytes of LiNO₃ and Li₂SO₄ which are typically less than 100 mS cm⁻¹. After the addition of Br₂ as the active electrode material, the ionic conductivity descends to some extent owing to the conversion of Br⁻ into Br₃⁻ or Br₅⁻, but the ionic conductivity is still superior to those of the non-aqueous electrolytes. For LiBr aqueous solution, the disappearance and the formation of Br₃⁻ (yellow) could be observed via the color change of the electrolyte solution and the measurement of UV-Vis spectra during the reduction and the oxidation processes (see Fig. S2). The glassy carbon (GC) electrode acting as the current collector for the positive electrode has a wide electrochemical stability window, which can be seen from the blank in Fig. 1(a) (see Supplementary Fig. S3 for its curve between -1.5 and 1.5 V (vs. SCE)). Even the scan rate is up to 1 mV/s, there are no evident redox peaks corresponding to the production of oxygen or hydrogen. It is superior to the metallic mesh current collectors²³ and carbon black electrode in alkali ion batteries using the Br₂/Br⁻ redox couple as reported²⁷, and the threshold potential of the O₂ evolution reaction is 4.4V (vs. Li⁺/Li). This clearly shows that oxygen evolution does not happen due to overpotentials even the theoretical potential for oxygen evolution (1.229 V vs. SHE) is very close to that for the oxidation of Br⁻. This is consistent with the former reports²⁷. From the cyclic voltammogram (CV, Fig. 1a) of 1.69 × 10⁻² mol L⁻¹ Br₃⁻ in

1 mol L⁻¹ LiBr aqueous solution has a good electrochemical performance. The CV curves at different scan rates reflect the good reversibility of the redox reaction of Br₃⁻/Br⁻, the cathodic peak current and potential at 0.1 mV s⁻¹ are 0.068 mA and 0.831 V (vs. SCE), respectively. The reduction peak potential declines slightly and the reduction peak current increases with the scan rate from 0.1 to 10 mV s⁻¹, suggesting the fast kinetics of Br₃⁻/Br⁻. It can also be confirmed by analyzing the CV response using the Randles-Sevcik equation^{11b},

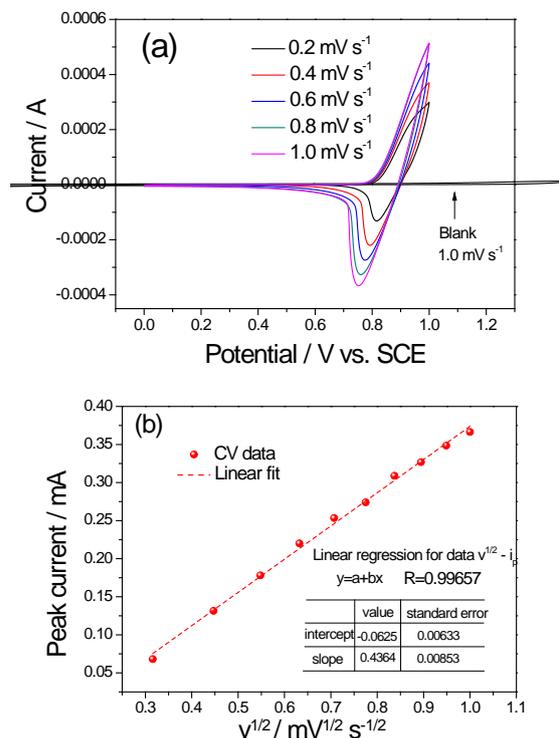


Fig. 1 (a) CV curves of 1 mol L⁻¹ LiBr aqueous solution containing 1.69 × 10⁻² M Br₃⁻ at different scan rates, (b) the changes of the cathodic peak-current from (a) with the scan rates. Blank in (a) was carried out by using 0.5 mol L⁻¹ Li₂SO₄ solution at 1 mV/s.

$$I_p = 0.4463(F^3/RT)^{1/2} n^{3/2} A D^{1/2} C v^{1/2} = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \quad (2)$$

where B is $2.69 \times 10^5 n^{3/2} A D^{1/2} C$, n is the number of electrons transferred in the redox process (here it is 2), A is the electrode area (here 0.07 cm²), F is the Faraday constant (in C mol⁻¹), D is diffusion coefficient (in cm² s⁻¹) and C is the concentration of Br₃⁻ ions (here about 1.69 × 10⁻² mol L⁻¹). According to equation (2), the plot of the reduction peak current I_p versus the square root of the scan rate ($v^{1/2}$) should be a straight line, which is shown in Figure 1b. It has a $y = a + bx$ linear trend and the b parameter can be calculated. Based on b parameter, the lithium diffusion coefficient was further calculated as 2.42×10^{-2} cm² s⁻¹. These results also reveal that the mechanism of Br₃⁻/Br⁻ reduction reaction is diffusion-controlled. Evidently, it is different from the intercalation compounds, and the diffusion coefficient is much higher than that of lithium ions in the lithium intercalation compounds which is generally below 10⁻⁸ cm² s⁻¹.³⁰⁻³² Of course, it is different from oxygen electrode for Li//air batteries, where oxygen diffusion coefficient in aqueous

electrolytes ($7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)³³, organic electrolyte ($1.67 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$)³⁴ or ionic electrolytes ($1.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)³⁵ is much lower and its concentration is also much lower.

From the repeated CVs (10 scans) at the scan rate of 0.5 mV s^{-1} (Fig. S4) it can be seen that the good overlapping of the anodic and cathodic peaks in the subsequent scans, which demonstrates that the bromine positive electrode is stable during the electrochemical reaction. When $1 \text{ mol L}^{-1} \text{ Br}_2$ in $7 \text{ mol L}^{-1} \text{ LiBr}$ solution was used to test the discharge rate performance of Br single electrode (Fig. S5), the average discharge potential is 0.87 V (vs. SCE) at the current density of 0.5 mA cm^{-2} , and the discharge voltage plateau only descends slightly when the current density increases. However, the voltage is still maintained at 0.71 V (vs. SCE) even at the current density of 5 mA cm^{-2} . Furthermore, the discharge plateau remains obviously very stable at different current densities. This further illustrates that the bromine redox reaction of the single electrode is stable, and indicates a good rate performance as well. This is superior to the lithium intercalation compounds and oxygen electrodes in terms of kinetics.

Electrochemical performance of aqueous Li//Br battery

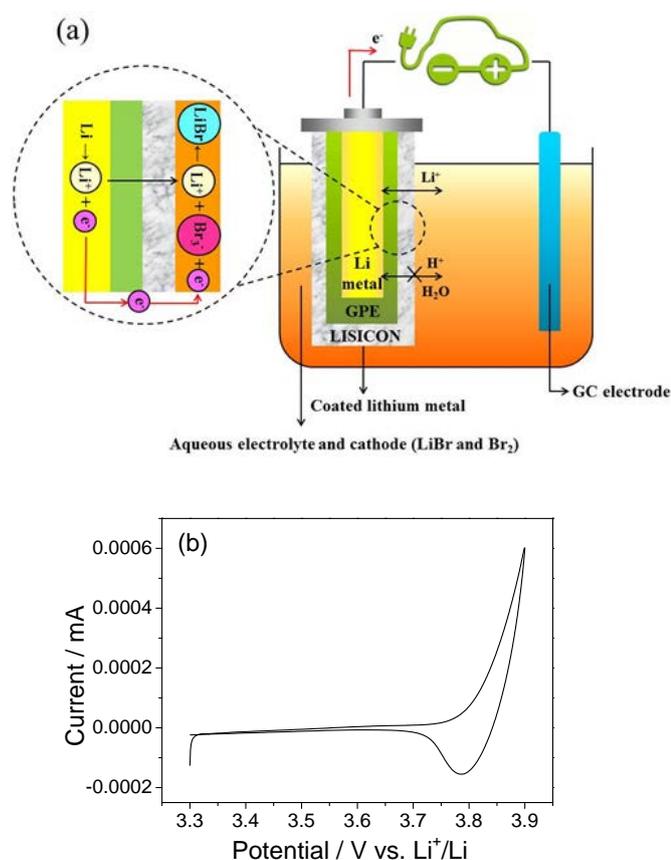
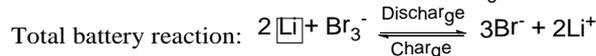
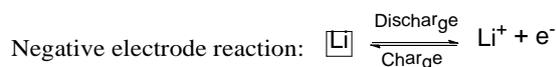


Fig. 2 (a) Schematic illustration of our rechargeable Li//Br battery composed of Li metal coated with GPE and LISICON as the negative electrode, aqueous LiBr solution (1 mol L^{-1}) as the electrolyte, and 0.1 mol L^{-1} liquid Br_2 or Br_3^- as the positive electrode with glassy carbon as the current collector, and (b) cyclic voltammogram (CV) of rechargeable Li//Br battery at the scan rate of 0.1 mV s^{-1} .

Based on the above discussion, Br single electrode based on $\text{Br}_3^-/\text{Br}^-$ redox couple can be a good positive electrode. Our former work shows clearly that the coated Li metal is stable in aqueous solution, and Li dissolution and plating can reversibly happen at about -2.70 V (vs. SCE) when it is immersed in aqueous solution.^{13,19} Even the crisp LISICON film is broken, the porous polymer matrix can only allow very slow contact of Li metal with water due to its hydrophobic characteristics and the safety and reliability of Li metal is much improved,^{19b} which is different from the others' work.^{10,16,20,22} Of course, direct contact of Li with Br_2 should be prevented if Li metal is used directly without coating. When they are combined together, another rechargeable battery system, Li//Br battery, can be established. Its structure is schematically illustrated in Figure 2a, which uses LiBr aqueous solution as electrolyte and glassy carbon as current collector for the positive electrode. Lithium metal is coated with a home-made gel polymer electrolyte (GPE) and a ceramic solid electrolyte (LISICON from Ohara Inc., Japan) film. Theoretically the work voltage of this battery is 4.12 V . The redox reactions of the assembled lithium/bromine (Li//Br) battery during the charge and discharge processes are shown as the following:



where the bracket for Li indicates that the Li metal is coated with the composite film.

CV curves at the scan rate of 0.1 mV s^{-1} for the rechargeable Li//Br battery is shown in Fig. 2b. During the discharge process, the current peak is situated at 3.78 V , corresponding to the reduction of Br_3^- to Br^- by getting electrons and the concurrent oxidation of Li to Li^+ ions by losing electrons at the negative electrode. At the same time, Li^+ ions pass through the GPE and LISICON film into the aqueous electrolyte. During the charge process, the reverse processes take place. The reduction curve above 3.80 V represents that Br^- is oxidized to Br_2 or Br_3^- , and Li^+ ions in the non-aqueous electrolyte pass across LISICON film and GPE from the aqueous electrolyte solution and deposit as metallic Li by getting electrons.

Figure 3a demonstrates the charge/discharge behavior of the Li//Br battery based on the 100% DOD of Br_2 by using $0.1 \text{ mol L}^{-1} \text{ Br}_2$ in $1 \text{ mol L}^{-1} \text{ LiBr}$ aqueous electrolyte. Its open-circuit voltage (OCV) is 4.09 V . When a current of 0.03 mA is applied, its voltage initially drops to 3.95 V . The discharge curve of the battery shows a relatively good plateau since there is no phase change in the discharge process²². The average voltage difference between the discharge and charge processes for the Li//Br battery is 0.19 V initially and slowly increases with the charging time to 0.29 V , which is far smaller than that of a Li//air battery ($> 1 \text{ V}$)⁹ due to much faster kinetics. It is similar to our 2nd generation aqueous rechargeable lithium batteries (2G ARLB), which can be charged and discharged in the voltage range of 3.7 and 4.25 V in $0.5 \text{ M Li}_2\text{SO}_4$ neutral solution with 100% Coulomb efficiency after the first cycle²². The increase in the charge/discharge voltage difference is from the change of Br_2 concentration, which can be well understood from the Nernst equation. An increase of about 0.1 V (from 0.19 to 0.29 V) suggests that the change of Br_2 concentration is

decreased about 100 times, indicating that Br_2 or Br_3^- is almost completely reduced. Its specific capacity is 335 mAh g^{-1} for Br_2 , which is higher than that of the Li- and Mn-rich Li_2MnO_3 positive electrode for lithium ion batteries and that reported for alkali ion batteries (303 mAh g^{-1}) as well²⁷.

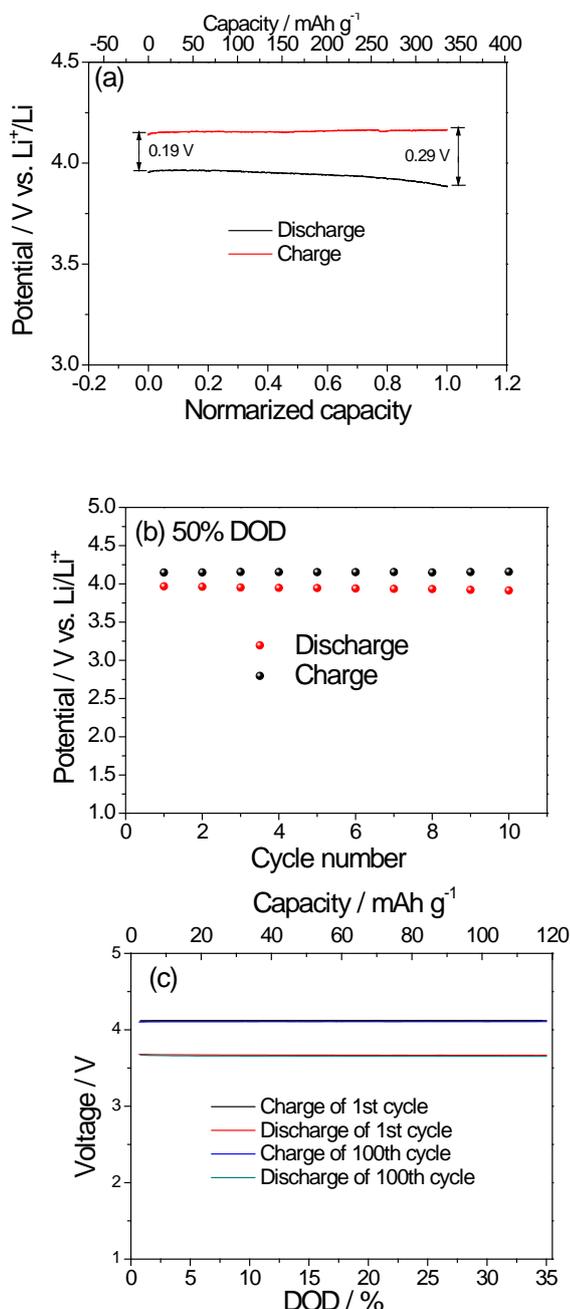


Fig. 3 Electrochemical behavior of Li//Br battery: (a) charge/discharge curves for 100% DOD of the Li//Br battery in which aqueous positive electrode is 1 mol L^{-1} LiBr with 0.1 mol L^{-1} Br_2 , (b) changes of voltage of charge and discharge process based on the 50% depth of discharge for 10 cycles, and (c) galvanostatic charge-discharge curves in the first and the 100th cycles of Li// 1 mol L^{-1} Br_2 with 7 mol L^{-1} LiBr battery at the current density of 4.2 mA cm^{-2} based on 35% DOD.

Furthermore, there is no significant average voltage fading and growth for discharge and charge during 10 cycles at 50% depth of discharge (DOD) (Figure 3b). It also shows a good platform with high voltage (Fig S5), which is superior to Li//S and Li//air batteries^{9,36}. The energy density based on the mass of Li metal and Br_2 is 1220 Wh kg^{-1} . In our battery system, water and LiBr are just like solvent and electrolyte supporting salt, which are similar to carbonate solvent and LiPF_6 in lithium ion batteries. They are not components of the positive electrode, liquid Br_2 .

Aqueous solution of 1 mol L^{-1} Br_2 with 7 mol L^{-1} LiBr as positive electrode and electrolyte, respectively, was also tested as a Li//Br battery. Figure 3c demonstrates the galvanostatic charge-discharge profiles for the 1st and the 100th cycles at the current density of 4.2 mA cm^{-2} at the fixed DOD of 35%. The charge and discharge voltages do not present evident change, only from 4.12 to 4.11 V and from 3.67 to 3.66 V, respectively, from the first cycle to the 100th cycle. The excellent profiles overlapping, as well as a small voltage gap between charge and discharge process assumes a very stable behavior and good cycling behavior of the Li//Br battery. The outstanding cycling performance can be ascribed to the following reasons: (1) the charge/discharge processes of Li//Br battery do not cause a volume change of the positive electrode since there is no phase change, which is superior to lithium intercalation compounds and other solid electrodes. The slow electrode kinetics relating to Li intercalation/deintercalation into/from its host materials also leads to low power density of lithium ion batteries; (2) the ceramic separator of LISICON, current collector and aqueous positive electrode are stable at the given operating condition. The operating potential is between 4.15 and 3.66 V, neither H_2 nor O_2 evolution is observed at the charge/discharge process despite that lithium metal has the lowest redox potential, -3.05 V (vs. standard hydrogen electrode, SHE). The main reason is that Li^+ ions acting as the charge transfer media which can cross over the hydrogen evolution potential range through LISICON from the aqueous solution and arrive at the lithium metal¹⁹; (3) the positive Br_3^- electrode is electrochemically stable²⁴; and (4) there is no significant structure and phase change of LISICON. Fig. S7 exhibits SEM morphology of the surfaces of the LISICON glass-ceramics separator before and after 100 cycles. Glass featured phase can be seen clearly. Well crystallized grains with average size of about 500 nm are present. The size of particle is reduced and the surface becomes uneven after 100 cycles, but glass featured phase is still well remained.

Figure 4a shows a polarization graph recorded in the range of current density from 0.42 to 12.7 mA cm^{-2} of a Li//Br battery using 1 mol L^{-1} Br_2 in 7 mol L^{-1} LiBr, which was tested for 5 mins at each current density (Figure S5). The discharge voltage can be up to 4.097 V at the low current density, which is very close to its theoretical potential. It decreases with the increase of the current density due to the larger internal resistance of the coating composite film for Li metal, whereas it still keeps 2.495 V even at the current density of 12.7 mA cm^{-2} . In the case of the single Br electrode, the voltage difference is less (Figure S6) in the same range of current density. This sharp large drop in discharge voltage indicates a mass transport resistance due to the slow mobility of lithium ions in the solid electrolyte¹⁶. Therefore, reduction in the resistance of the solid electrolyte would dramatically improve the battery performance¹³, indicating the demand for the design of a superior solid electrolyte. Its power density increases with the current density. At the current density of 12.3 mA cm^{-2} , it reaches its maximal

power density 29.7 mW cm^{-2} with a corresponding average discharge voltage of 2.495 V . These results are similar to those of Li/I battery and better than those based on aqueous positive electrode of $\text{Fe}(\text{CN})_3/\text{Fe}(\text{CN})_6^{4-}$ (Table S1) due to the easier gain/loss of electrons for $\text{Br}_3^-/\text{Br}^-$ redox couple. The discharge performance of Li//Br battery at different current densities can be seen from Figure 4b, and the battery shows still a flat plateau. Its performance became poor when the current density is larger than 9 mA cm^{-2} because of the large resistance of the solid electrolyte, which cannot provide enough lithium ions.²²

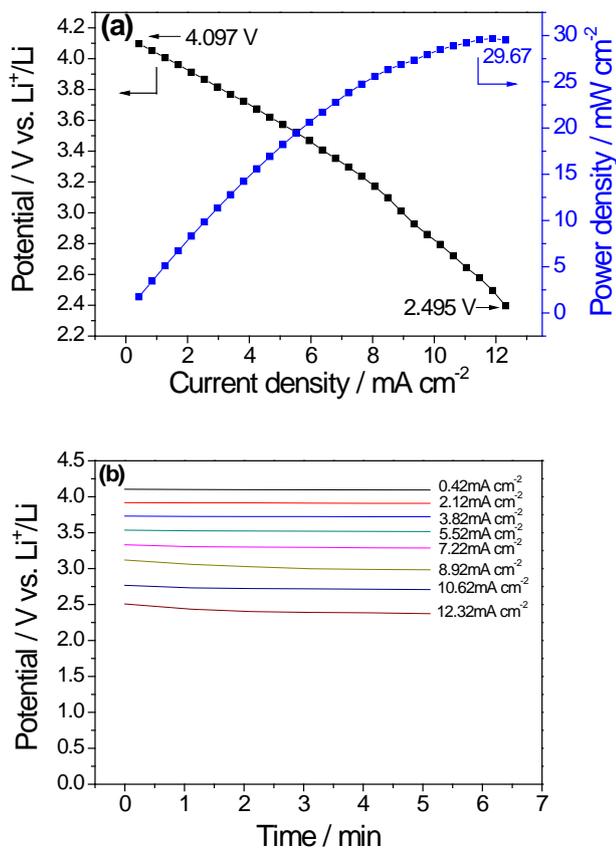


Fig. 4 (a) Polarization graph presenting discharge potential and corresponding power density of a Li//Br battery using $1 \text{ mol L}^{-1} \text{ Br}_2$ solution with $7 \text{ mol L}^{-1} \text{ LiBr}$ at different current densities from 0.42 to 12.74 mA cm^{-2} , and (b) discharge behavior of the Li//Br battery at different current densities.

In the previous work,²² the iodide/triiodide redox couples are used which have a suitable reaction potential (0.536 V versus SHE) in an aqueous positive electrode for the Li/I battery. The tribromide/bromide is more advantageous at the standard response voltage (1.05 V vs. SHE). What's more, Br^- is more stable than I^- which can be easily oxidized by oxygen when exposed to air. Salt of bromide is much cheaper than that of iodide as the electrolyte. As mentioned above, our coated lithium metal has an improved safety and reliability.^{19b} Based on the traditional manufacturing technologies for batteries, if 40%-50% of the estimated energy density based on the electrode masses can be utilized,¹² it means that the practical energy density would be above 500 Wh kg^{-1} . In addition, the density of Br_2 is 3.119 g cm^{-3} . This indicates that an electric car based on this Li//Br battery could run at least 500 km for one

charge, which is comparable with those of most engine cars, since the present technology based on lithium ion batteries can run about 160 km for one charge at the energy density of about 120 Wh kg^{-1} ^{9a}.

Furthermore, Br-based electrodes have already shown some applications in redox flow batteries such as Zn//Br for large scale electrical energy storage due to their advantages of long cycling life, low cost of maintenance, flexible design and high efficiency²⁶. There are many obvious differences between our rechargeable Li//Br battery and conventional non-aqueous lithium bromine battery, which is accompanied with the challenge of bromine's chemical reactivity with the separator resulting in the problem of self-discharge, complex component and complicated configuration of cell, as well as the limited bromine solubility and insufficient ionic conductivity in the organic electrolyte. The latter could not provide practically available rate and capacity for applications in early cardiac pacemakers. The inspiring results have also shown promising application in flow-through batteries^{37,38}.

Conclusions

In conclusion, the $\text{Br}^-/\text{Br}_3^-$ redox reaction-operated aqueous Li//Br battery exhibits prominent cycling performance with considerable energy and power densities. More importantly, the discharge voltage of the battery is high (3.96 V) and very stable, without degradation during the discharge process. The specific energy density (1220 Wh kg^{-1}) based on two electrodes is much attractive in comparison to the conventional lithium ion batteries. Small polarization for the positive electrode and long cycling life are of great attraction for practical application. It is different from the former batteries based on bromine, lithium ion battery and other high energy density systems such as Li//air and Li//S batteries. Low cost and reliable safety make Li//Br battery as a good platform for post lithium ion batteries.

Acknowledgements

The research was supported by China National Funds for Distinguished Young Scientists, NSFC (21073046 and 21374021) and STCSM (12JC1401200 and 14520721800).

Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [Ionic conductivity of aqueous positive electrode, changes of LiBr solution before and after charge, electrochemical window of GC electrode, Stability of Br electrode and LISICON, discharge voltage curves in different current density and comparison between different aqueous rechargeable lithium batteries]. See DOI: 10.1039/b000000x/

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