



A novel hybrid positive electrode with liquid-solid redox couples having high-capacity for lithium battery

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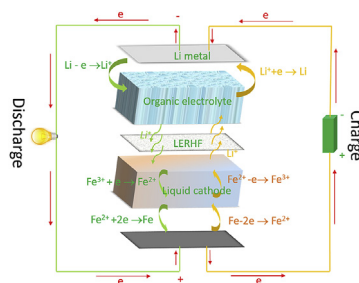
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HIGHLIGHTS

- A hybrid positive electrode of $\text{Fe}^{3+}/\text{Fe}^{2+}/\text{Fe}$ in N,N -Dimethylformamide is evaluated.
- An impermeable protective film with a high lithium ion conductivity is used.
- The positive electrode exhibits an excellent cycling performance with a high capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

We demonstrate a novel rechargeable energy storage system having a metallic lithium negative electrode and a liquid–solid hybrid positive electrode of $\text{Fe}^{3+}/\text{Fe}^{2+}/\text{Fe}$ in N,N -Dimethylformamide, which are separated by an impermeable NASICON-type $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ge}_{0.2}\text{Ti}_{1.4}(\text{PO}_4)_3$ -epoxy resin composite film with a lithium ion conductivity of ca. $5.0 \times 10^{-4} \text{ S cm}^{-1}$. The discharge curve for the battery shows two plateaus. The first plateau corresponds to $\text{Li} + \text{FeCl}_3 = \text{LiCl} + \text{FeCl}_2$, while the second one is associated with $2 \text{Li} + \text{FeCl}_2 = 2 \text{LiCl} + \text{Fe}$. In the process of reduction of Fe^{3+} to Fe^{2+} , it delivers a stable discharge capacity of ca. $110 \text{ mAh g}_{\text{FeCl}_3}^{-1}$ with a Coulombic efficiency higher than 95% and is capable of enduring over 60 circles at a high current density of 1.0 mA cm^{-2} without any catalyst. Furthermore, a stable discharge capacity up to ca. $455 \text{ mAh g}_{\text{FeCl}_3}^{-1}$ is achieved for conversion of $\text{FeCl}_3/\text{FeCl}_2/\text{Fe}$ with a three-electron reaction. This work demonstrates a proof of feasibility of hybrid liquid–solid hybrid positive electrode, since these reactions are reversible confirmed by x-ray diffraction patterns and EDX mapping test.

1. Introduction

Building electric vehicles (EVs) with high-capacity rechargeable batteries instead of internal-combustion engine is considered as an effective way to reduce the consumption of fossil energy [1,2]. Up to now, many new types of lithium-metal batteries (LMBs) beyond lithium-ion batteries (LIBs) have been proposed, such as Li-O_2 and Li-S

rechargeable batteries [3–6]. The Li-S battery promises to meet the target of a 500 km range for EVs in view of its high theoretical energy density (ca. 2510 Wh kg^{-1} and 2199 Wh L^{-1}) [7]. However, rapid capacity fading owing to the well-known shuttle effect by the reactions of various soluble polysulfide intermediates with Li -metal negative electrode must be addressed [8,9]. Similarly, the calculated energy densities of rechargeable non-aqueous Li-O_2 battery system including

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oxygen are as high as 3505 Wh kg^{-1} [10]. However, non-aqueous Li–O₂ batteries still face some formidable challenges, including the sluggish oxygen reduction/evolution reaction kinetics, plus side reactions between the strong oxidizing discharge products (Li₂O₂/LiO₂) and electrolyte/carbon/binder [11–13]. Recently, Goodenough et al. proposed a new concept of aqueous positive electrode using a redox couple of Fe(CN)₆^{3−}/Fe(CN)₆^{4−} for next-generation alkali-ion batteries [14,15], which was further branched out by Zhao et al. They used I₃[−]/I₂ [16], Br[−]/Br₂ [17], Fe(C₅H₅)₂/[Fe(C₅H₅)₂]⁺ [18] as redox couples of fluid positive electrodes, respectively, which all exhibited excellent rate capacities. However, there is no great advantage for the specific capacity of these fluid positive electrodes due to a one–electron reaction, in comparison with that of the common positive electrode materials of commercial LIBs.

The energy density of battery is significantly determined by the electrode capacities and potential difference between positive and negative electrodes. The capacity of electrode is decided by the transfer number of electron per molecule and mole mass, while the potential difference is dependent on their Fermi energy. Given all this, in this work, we propose a radical but facile hybrid liquid–solid redox couple as the positive electrode for LMBs, in order to improve the capacity drastically by increasing transfer number of electron per molecule.

Fig. 1 demonstrates the theoretical potential of various hybrid liquid–solid redox couples versus standard hydrogen electrode (SHE). Numerous redox couples have the potential to perform as the positive electrodes for the unique LMBs, because Li metal negative electrode has the lowest electrochemical potential (−3.04 V vs. SHE). The theoretical specific capacities and potential (vs. Li/Li⁺) of various hybrid redox couples are summarized in Table S1, which are calculated based on the metallic chlorides due to excellent solubility and low molecular mass. Among these materials, it is obvious that the three–electron redox couple of FeCl₃/Fe²⁺/Fe has advantages in terms of high theoretical potential and capacity of 3.81 V and 496 mA h g^{−1}, respectively. Additionally, FeCl₃/Fe²⁺/Fe is inexpensive, abundant on earth and environmentally benign. Thus, we are committed to demonstrating the feasibility of redox couple of Fe³⁺/Fe²⁺/Fe in solutions as a positive electrode for LMBs.

It is noteworthy that one of the crucial components of this battery system is the impermeable solid lithium–ion conducting electrolyte so as to keep both electrodes apart. The commercial impermeable LISICON film (Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O₁₂) is only supplied by Ohara Inc. Japan, which has a thickness of 150–250 μm with an excellent bending strength (4 points) of 140 N/mm² [19]. However, its low ionic conductivity (ca. $1.0 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C) and high cost are the bottleneck for the commercialization of LMBs with fluid positive electrode. In our previous study, a water–impermeable hybrid sheet of LAGTP (Li_{1.4}Al_{0.4}Ge_{0.2}Ti_{1.4}(PO₄)₃) and epoxy resin film with a high ionic conductivity of $5.26 \times 10^{-4} \text{ S cm}^{-1}$ and bending strength (3 points) of

120 N/mm² has been already invented [20], and successfully used in the aqueous lithium–air batteries as a solid electrolyte separator. Herein, the LAGTP–epoxy resin hybrid film (denoted as LERHF) is used in the novel battery system as the impermeable separator to block fluid positive electrode.

2. Experimental

2.1. Preparation of LERHF

The fabrication process of LERHF is shown in the flowchart (see Fig. S1 in the ESI). LAGTP powders prepared using a sol–gel method reported previously [21] were dispersed in a mixed solution of ethanol and toluene with binder and plasticizer to form a tape-casting slurry by ball milling for 24 h. Then the slurry was tape-casted, and the green sheets were dried, cut, laminated and sintered at 900 °C for 7 h sequentially. Finally, the LERHF was obtained by dropping a mixed solution of 1 M 1,3-phenylenediamine and 2 M 2,2-bis(4-glycidylphenyl)propane in tetrahydrofuran on the LAGTP sheet surface, followed by a heat treatment at 150 °C for 24 h. The LERHF must be polished to remove the residual epoxy resin polymer on the surface (see Fig. S1 in the ESI) after polymerization (See Fig. S2 in the ESI) to improve the ionic conductivity.

3. Material characterization

The X–ray diffraction (XRD) patterns were obtained using a Rigaku Rint 2500 diffractometer with a Cu Kα radiation in the 2θ from 10° to 90° at a scanning rate of 0.02° s^{−1}. The morphology of discharge products was investigated using a field emission scanning electron microscope (FESEM, Carl Zeiss Jena Utral 55) coupled with an energy dispersion X–ray spectrometer (EDX).

3.1. Preparation of fluid positive electrode

All the chemicals used in the experiments were of analytical grade. Anhydrous FeCl₃ (Aladdin) and LiCl (Aladdin) were further dried in an Ar–filled glove box (O₂ < 0.5 ppm, H₂O < 0.5 ppm) at 100 °C for 24 h. All organic solvents (e.g. 1-propanol, ethylene glycol, ethanol, acetone, DMF, toluene) were dehydrated by soaking 4 Å sieves (Aladdin) for at least one week. Then the fluid electrodes were prepared by dissolving pre-weighing FeCl₃ and LiCl in various organic solvents and deionized water under magnetic stirring for 2 h.

3.2. Assembly of the battery

We noticed that the aqueous positive electrodes reported previously were usually circulated by a pump to enhance utilization efficiency of active materials [14,16]. Unfortunately, the architecture of this battery system is too complicated, resulting in a low practical specific mass/volume energy density. Consequently, it is logical to simplify the architecture of the battery, where the fluid positive electrode is flowed by itself instead of the pump. The battery performance was measured using a Swagelok–type cell designed by our engineer (Fig. 2). A lithium metal disk (φ12.0 mm) attaching to a steel column was used as a negative electrode and current collector, respectively. With regard to the positive electrode, the aforementioned solutions were injected into one side of cell using a disposable syringe, and then the injection hole was plugged up. A titanium column clad with a hydrophobic carbon paper disk (φ12.0 mm) served as a current collector and supporter of discharge products. The conventional non-aqueous electrolyte consisting of ethylene carbonate (EC) and diethylene carbonate (DEC) (1:1 v/v) with 1 M LiPF₆ soaked in a glass fiber (GF/A, Whatman) was employed as a buffer layer to prevent the direct contact of lithium metal with LERHF, because NASICON–type lithium–ion conducting electrolyte is unstable to lithium metal [22]. The LERHF combined with a pair of rubber rings

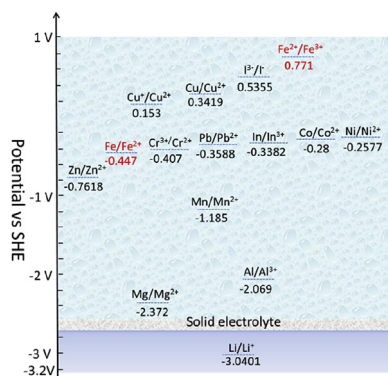


Fig. 1. Diagram of the potentials of various liquid–solid hybrid redox couples versus SHE.

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