

Supporting Information

**High-Voltage Aqueous Battery Approaching 3 V Using an
Acidic/Alkaline Double Electrolyte**

Long Chen, Ziyang Guo, Yongyao Xia¹ and Yonggang Wang**

Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Institute of New Energy, Fudan University, Shanghai 200433, China.

* **Corresponding author.** Tel & Fax: 0086-21-51630318

E-mail address: yyxia@fudan.edu.cn; ygwang@fudan.edu.cn

Experimental Section:

Ceramic LATSP films ($2.5 \times 2.5 \text{ cm}^2$; $150 \mu\text{m}$ in thickness) is the product of Ohara (Japan), and were used as received. Pt-plate ($1 \times 1 \text{ cm}^2$), Zn-plate ($1 \times 1 \text{ cm}^2$) and Titanium Mesh ($1 \times 1 \text{ cm}^2$) were used as electrodes for different electrochemical investigations.

Electrochemical impedance spectroscopic (EIS) measurement: Two Pt-plate electrodes ($1 \times 1 \text{ cm}^2$) were symmetrically placed into two 1 M H_2SO_4 solutions separated by an LATSP film or two 1 M Li_2SO_4 solutions separated by an LATSP film. The EIS measurement was performed at the cell's open circuit voltage (OCV) in the frequency range of 10^6 – 0.01 Hz with an AC signal amplitude of 10 mV. A Solartron instrument model 1287 with an electrochemical interface and 1255B frequency response analyser was employed for the EIS measurements.

Zn/ KMnO_4 cell measurement: The Zn anode and Ti mesh ($1 \times 1 \text{ cm}^2$) were placed into the 2 mL alkaline electrolyte (2 M KOH + 2 M LiOH) and 2 mL acidic electrolyte (1 M H_2SO_4 + 2.7 mg KMnO_4), which were separated by an LATSP film. The OCV and discharge tests were performed using a Solartron instrument model 1287. The discharge current density (mA/g) and the discharge capacity (mAh/g) were calculated based on the mass (2.7 mg) of KMnO_4 in the acidic solution. In these investigations, the Zn anode was in excess.

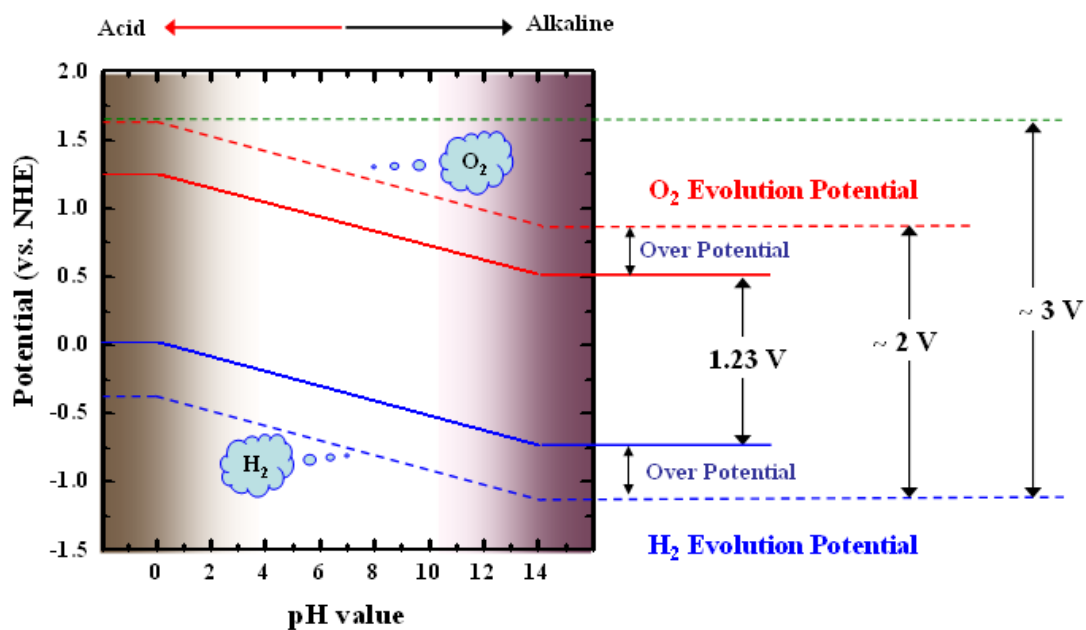


Fig. S1 Stable potential window of H₂O at various pH values

As shown in **Fig. S1**, the potential for O₂ (or H₂) evolution reduces with increasing pH. If we can combine the high O₂ evolution potential from an acidic aqueous electrolyte solution with the low H₂ evolution potential from an alkaline aqueous electrolyte solution, the total electrochemically stable potential window could be as wide as ~3 V, which is comparable to that of a non-aqueous organic electrolyte solution (see **Fig. S1**).

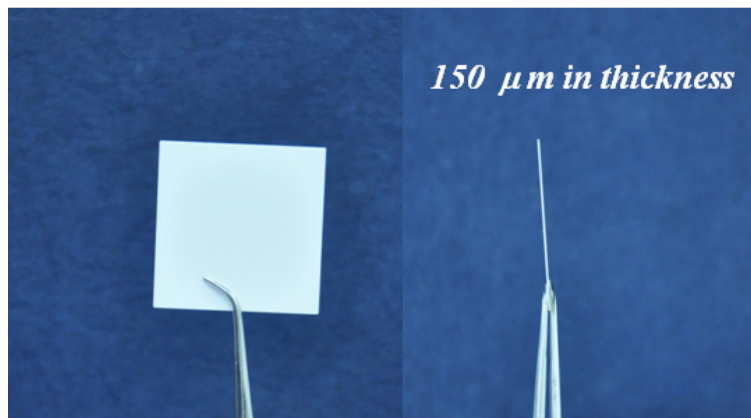


Fig. S2 Photograph of LATSP ceramic film (seen from different angles). The water-stable lithium super-ionic conductor ceramic film (LATSP, $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$) with thickness of 0.15 millimeter is the product of Ohara Inc., Japan. Its conductivity is $10^{-4} \text{ S cm}^{-1}$. LATSP is a kind of ceramic solid electrolyte for lithium-ion batteries, and has been widely investigated on the study about all solid state lithium-ion batteries^[RS 1-3] and aqueous Li-air battery^[RS 4].

- RS 1. J. W. Fergus, *J. Power Sources*, 2010,195,4554-4569.
RS 2. J. Xie, N. Imanishi, T. Zhang, A. Hirano, Y. Takeda, O. Yamamoto, *J. Power Sources* 2009,189,365–370.
RS 3. C. Yada, Y. Iriyama, T. Abe, K. Kikuchi, Z. Ogumi, *Electrochem. Commun.* 2009, 11, 413–416.
RS 4. a) P. G. Bruce, S. A. Frreunberger, L. J. Hardwick, J. M. Tarascon, *Nater. Mater.* 2012,11,19-29; b) Ding, F. *et al. J. Power Sources*, 214, 292-297(2012).

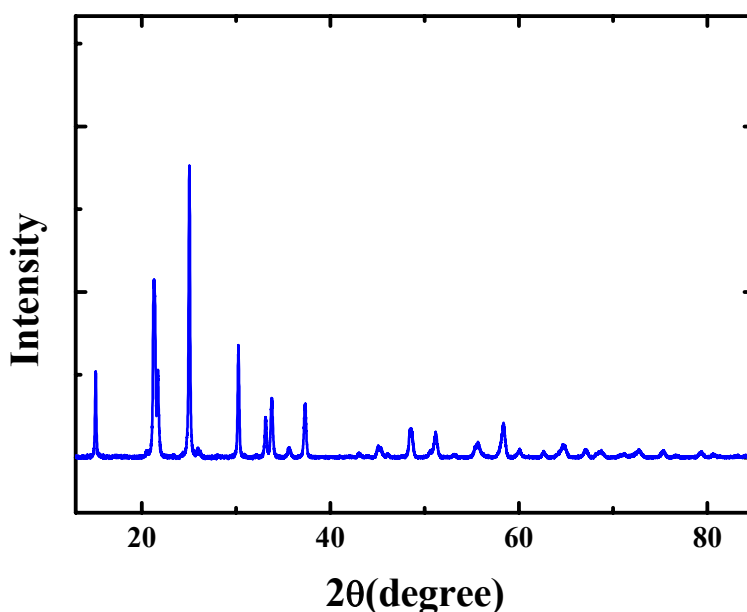


Fig. S3 The XRD patterns of LATSP ceramic film. LATSP is a kind of ceramic solid electrolyte for lithium-ion batteries, and has a typical NASICON structure (See

Fig. S3 . The NASICON structure consists of PO_4 -tetrahedra and MO_6 -octahedra ($\text{M}=\text{Ti}$) linked by shared oxygen atoms ^[RS 5-8]. There are two types of position of Li-ion localization that can be distinguished: M1 positions, surrounded by six oxygen atoms; and M2 positions, surrounded by eight oxygen atoms. Hence, a system of three dimensional channels arises, where Li-ion transport realized by alternating of positions M1 and M2 ^[RS 5,6] (see **Fig. S4**) . Accordingly, the ceramic LATSP film can permit the pass of Li-ion with high diffusion rate.

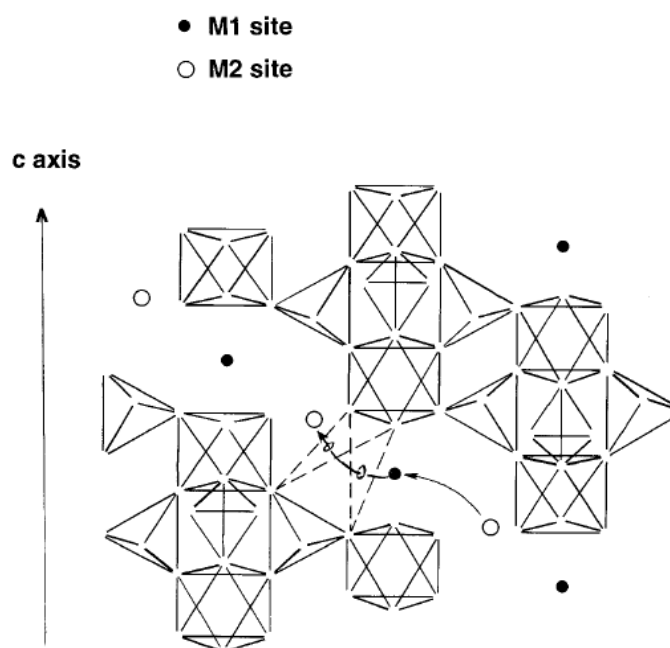


Fig. S4 Schematic view of the NASICON structure in rhombohedral symmetry (Obtained from RS6).

- RS 5: I. Y. Pinus, A. V. Khoroshilov, K. S. Gavrichev, V. P. Tarasov, A. B. Yaroslavtsev, *Solid State Ionics*, 2012,212,112-116.
- RS 6: M. Cretin, H. Khireddine, P. Fabry, *Sensors and Actuators B*, 1997, 43,224-229.
- RS 7: A. Aatiq, M. Ménétrier, L. Croguennec, E. Suard, C. Delmas, *J. Mater. Chem.*, 2002, 12, 2971-2978.
- RS 8: K. Arbi, A. Kuhn, J. Sanz, F. Garacia-Alvarado, *J. Electrochem. Soc.*, 2010, 157, A654 -A659.

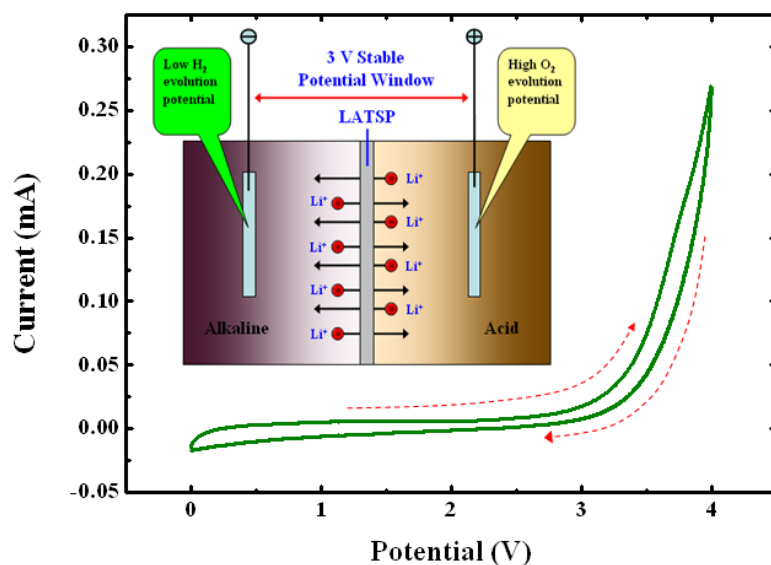


Fig. S5 CV curve at a sweep rate of 5 mV/s in the potential window from 0 to 4.0 V for the acid/LATSP/alkaline electrolyte. Two Pt-plate electrodes ($1 \times 1 \text{ cm}^2$) were symmetrically placed into the (1 M H_2SO_4 + 1 M Li_2SO_4)/LATSP/ (2 M KOH + 2 M LiOH) electrolyte for the CV test.

Cyclic voltammetry (CV) experiments were carried out at a sweep rate of 5 mV/s to examine the stable potential window of the acid/LATSP/alkaline electrolyte (see **Fig. S5**). During the CV test, two Pt-plate electrodes ($1 \times 1 \text{ cm}^2$) were symmetrically placed into the acidic electrolyte containing Li^+ (1 M H_2SO_4 + 1 M Li_2SO_4) and the alkaline electrolyte containing Li^+ (2 M KOH + 2 M LiOH) (**inset in Fig. S5**). During the positive sweep process, the Li^+ diffuses from the acidic electrolyte solution to the alkaline electrolyte solution through the ceramic LATSP film. The negative sweep process is the reverse of the positive sweep process. As shown in **Fig. S5**, the obvious cathodic current from the decomposition of the electrolyte occurs above 3 V, indicating that the acid/LATSP/alkaline electrolyte has a wide stable potential window of ~ 3 V. The system can utilize the high O_2 evolution potential from the acidic electrolyte solution and the low H_2 evolution from the alkaline electrolyte to realize a wide electrochemically stable potential window.

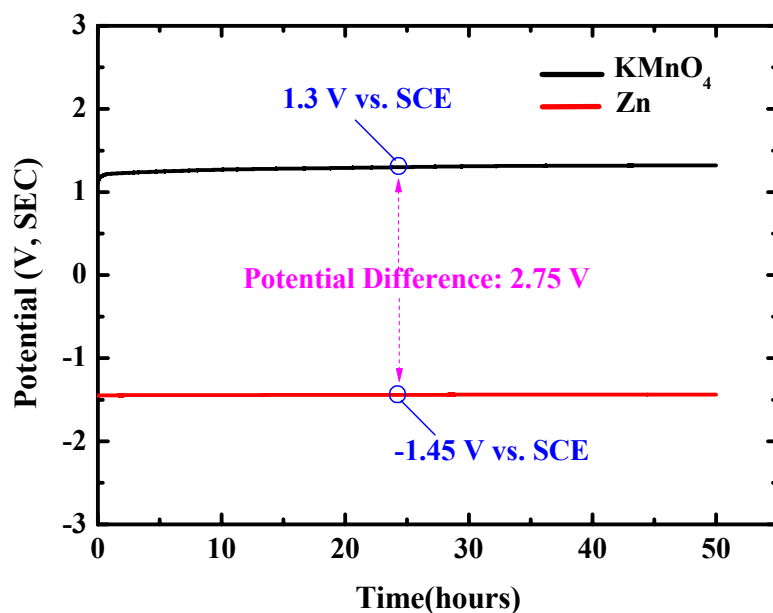


Figure S6 Open circuit Potential (OCP) investigation of KMnO_4 cathode and Zn anode by three-electrode system, where Pt-Plate ($1 \times 1 \text{ cm}^2$) and Saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. [Ti-mesh ($1 \times 1 \text{ cm}^2$) was put in 20 mL acidic electrolyte (1 M H_2SO_4) containing KMnO_4 as work electrode for OCP investigation of KMnO_4 ; Zn-plate electrode was put in 20 mL alkaline electrolyte (2M KOH + 2MLiOH) as work electrode for OCP investigation of Zn.]