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## Base-Acid Hybrid Water Electrolysis

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Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

**A base-acid hybrid electrolytic system with a low onset voltage of 0.78 V for water electrolysis was developed by using a ceramic Li-ion exchange membrane to separate oxygen-evolving reaction (OER) in a basic electrolyte solution containing Li-ion and hydrogen-evolving reaction (HER) in an acidic electrolyte solution.**

Splitting water into hydrogen ( $H_2$ ) and oxygen ( $O_2$ ) is an attractive approach to convert solar energy into a fuel, and thus a number of strategies for the solar-driven splitting of water are being pursued with varying level of success.<sup>1–11</sup> The electrolysis of water coupled with current established solar electricity technology is one of the front-running technologies for storing electrical energy and converting it to  $H_2$  fuel. Water electrolysis may be performed under basic or acidic conditions,<sup>12</sup> or at neutral pH.<sup>6</sup> Despite the pH values, electrolytic water splitting requires an applied voltage of at least 1.23 V to provide the thermodynamic driving force. Because of the practical overpotentials associated with the reaction kinetics, a substantially larger voltage is inevitably needed, which explains why current electrolyzers typically operate at a voltage of 1.8 to 2.0 V.

The water-electrolysis reaction can be divided into two half-reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), both of which are crucial for the overall efficiency of water-splitting. The total driving voltage for water-electrolysis depends on the potential difference between OER and HER. Center of the research endeavors is the development of HER and OER electro-catalysts to increase the reaction rate and reduce the onset potential of water electrolysis.<sup>13–38</sup> A variety of materials have been robustly investigated, such as Co-based catalysts,<sup>6,13–18</sup> rare metal oxide based catalysts,<sup>19,20</sup> Ni-based catalysts<sup>21,22</sup> for the OER catalysis, and Pt,<sup>23</sup>  $MoS_2$ ,<sup>24</sup>  $C_3N_4$ ,<sup>25</sup>  $CoSe_2$ <sup>26</sup> and W-based catalysts<sup>27,28</sup> for the HER catalysis. However, despite progress in the

past decade, these catalysts do not exhibit a striking performance of increasing the efficiency.

On the other hand, it is well known that the potentials for OER and HER reduce with the increase of pH value of electrolyte solution (see supplementary Fig. S1). If we can combine the high HER potential in an acidic electrolyte solution with the low OER potential in a basic electrolyte solution, the overall driving voltage (= Potential<sub>OER</sub> – Potential<sub>HER</sub>) would be lower than the theoretical one (1.23V) (see supplementary Fig. S1). However, up to present, little effort has been expended for this purpose because the coexistence of an acid and a base in an electrolytic system is almost impossible. Accordingly, current water electrolysis can only be performed either in basic electrolyte solution or in acidic electrolyte solution.

In present work, we develop a base-acid hybrid electrolytic system that successfully combines the OER in a basic electrolyte solution with the HER in an acidic electrolyte solution through a ceramic Li-ion exchange membrane. Benefitting from the low OER potential in the basic electrolyte solution and the high HER potential in the acidic electrolyte solution, this system exhibited a

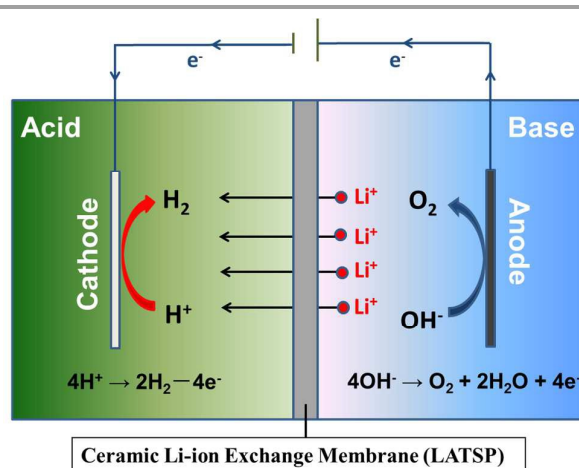


Fig. 1 Schematic illustration of the structure and operating principles of base-acid electrolytic cell.

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† Electronic Supplementary Information (ESI) available: Full experimental details and characterization of as prepared materials, Potentials of oxygen-evolving reaction (OER) and hydrogen-evolving reaction (HER) in aqueous electrolyte solutions with different pH values, additional information about LATSP film and solar cells. See DOI: 10.1039/x0xx00000x

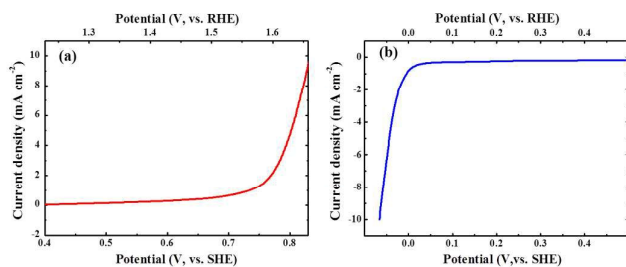


Fig. 2 (a) Linear sweep voltammetric data of CoO-nanowire-based film electrode ( $0.16 \text{ cm}^2$ ) in  $1 \text{ M KOH}$  with a sweep rate of  $5 \text{ mV s}^{-1}$ . (b) Linear sweep voltammetric data of Pt-foil electrode in  $0.5 \text{ M H}_2\text{SO}_4$  with a sweep rate of  $5 \text{ mV s}^{-1}$ . [Both experiments were performed with three-electrode method. A Pt-foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.]

low onset voltage of  $0.78 \text{ V}$  for electrolysis.

As shown in Fig. 1, the base-acid hybrid electrolytic cell includes a basic electrolyte solution containing Li-ions for OER, an acidic electrolyte for HER and a ceramic Li-ion exchange membrane ( $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ , LATSP) to separate basic and acidic electrolytes. Herein, the ceramic LATSP is a commercialized solid-state electrolyte film for Li-ion batteries (see supplementary Fig. S2 and Fig. S3). Our recent investigations about double-electrolyte batteries or fuel cell<sup>39-42</sup> have demonstrated that the ceramic LATSP film can permit the passage of Li-ion with a high diffusion rate, but prevent the passage of proton ( $\text{H}^+$ ) or  $\text{OH}^-$ . Operation of the hybrid electrolytic system depends on OER in a basic electrolyte solution ( $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$ ) and HER in an acidic electrolyte solution ( $4\text{H}^+ \rightarrow 2\text{H}_2 - 4\text{e}^-$ ), accompanied by Li-ion diffusion from basic electrolyte to acidic electrolyte through the ceramic LATSP film. The electrons, of course, pass around the external circuit (Fig. 1).

In this investigation, CoO nanowires and Pt-foil are used as the catalyst for OER in basic electrolyte solution and the catalyst for HER in acidic electrolyte solution, respectively. Prior to the fabrication of hybrid electrolytic cell, the onset potential of OER on CoO-nanowire-based film electrode in basic electrolyte solution and the onset potential of HER on Pt-foil-electrode in acidic electrolyte solution were investigated by linear sweep voltammetric measurement with typical three-electrode method. CoO nanowires were prepared according to previous report<sup>18</sup> (see Experimental Section for detail). X-ray diffraction (XRD) pattern, scanning electron microscope (SEM) image and transmission electron microscope (TEM) image of CoO nanowires are given in supplementary Fig. S4 and S5. The as-prepared CoO powder (80 wt %) was mixed with conductive agent (acetylene black, 10 wt %) and polytetrafluoroethylene (PTFE) binder (10 wt %) to form a film, which was then pressed onto a stainless steel mesh to form the CoO-nanowire-based catalytic electrode ( $0.16 \text{ cm}^2$ ) for OER (see experimental section for detail). Commercialized Pt-foil was used as the catalytic electrode for HER directly. Linear sweep voltammetric measurement of the CoO-nanowire-based electrode in the basic electrolyte solution ( $1 \text{ M KOH}$ ) is carried out with a sweep rate of  $5 \text{ mV s}^{-1}$  (Fig. 2a). It can be detected that the onset potential of OER is  $0.78 \text{ V}$  (vs. standard hydrogen electrode, SHE) or  $1.61 \text{ V}$  (vs. reversible hydrogen electrode, RHE), which is consistent with recent

report about CoO catalyst for OER in a basic electrolyte solution<sup>14</sup>. Fig. 2b gives the linear sweep voltammetric curve of Pt-foil electrode in the acidic electrolyte solution ( $0.5 \text{ M H}_2\text{SO}_4$ ) with a sweep rate of  $5 \text{ mV s}^{-1}$ , and it can be observed from Fig. 2b that the onset potential of HER is  $0 \text{ V}$  (vs. SHE or RHE).

Based on the above exploration, we assume that the base-acid hybrid electrolytic cell could exhibit an onset voltage of  $0.78 \text{ V}$  for electrolysis, when operated with a CoO-nanowire-based film electrode for OER and a Pt-foil electrode for HER, respectively. In order to prove this point, we fabricate a base-acid hybrid electrolytic cell, in which the CoO-nanowire-based electrode in a basic electrolyte ( $1 \text{ M KOH} + 0.5 \text{ M Li}_2\text{SO}_4$ ) and the Pt-foil electrode in an acidic electrolyte ( $0.5 \text{ M H}_2\text{SO}_4$ ) are separated by a ceramic LATSP. Onset voltage for electrolysis of the base-acid hybrid electrolytic cell was probed by linear sweep voltammetric measurement with two-electrode method (CoO-nanowire-based electrode was used as work electrode; Pt-foil electrode was used as counter/reference electrode.). The linear sweep voltammetric data at a sweep rate of  $5 \text{ mV s}^{-1}$  of this cell indicates that the electrolysis proceeds at about  $0.78 \text{ V}$  (Fig. 3a), which is consistent with above assumption. The Tafel plot is shown in Fig. S6 to characterize the electrolysis rate. It can be observed that this hybrid electrolytic system yields a Tafel slope of  $99.9 \text{ mV/decade}$ , indicating that the reaction rate is low. Stability of this cell was investigated by chronoamperometric measurements at  $1.0 \text{ V}$ . As shown in Fig. 3b, at the driving voltage of  $1.0 \text{ V}$ , a constant current of  $4 \text{ mA cm}^{-2}$  is well maintained for 24h, with bubbles continuously evolved and released from the surface of both electrodes.

As shown in above results, this architecture benefits from the low OER potential in basic electrolyte solution and the high HER potential in acidic electrolyte solution, and thus requires a low driving voltage for electrolysis. The novelty and advantage arise from the ceramic Li-ion conductive film (LATSP) that combines the OER in basic electrolyte solution and the HER in acidic electrolyte by using Li-ion for charge transfer. It should be noted that the Li-ion conductivity ( $10^{-4} \text{ S cm}^{-1}$ ) of ceramic LATSP is still low, which inevitably limits the electrolysis rate. As mentioned in beginning, the conventional electrolysis of water coupled with current established solar electricity technology is one of the front-running technologies for storing electrical energy and converting it to  $\text{H}_2$  fuel. However, as the lower power loads that is characteristic of solar

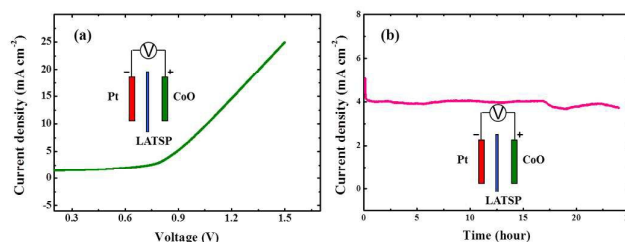


Fig. 3 Electrochemical performance of base-acid hybrid electrolytic cell [In this electrolytic cell, the CoO-nanowire-based electrode in a basic electrolyte ( $1 \text{ M KOH} + 0.5 \text{ M Li}_2\text{SO}_4$ ) and the Pt-foil electrode in an acidic electrolyte ( $0.5 \text{ M H}_2\text{SO}_4$ ) are separated by a ceramic LATSP.]. (a) Linear sweep voltammetric data achieved with two-electrode method at a sweep rate of  $5 \text{ mV s}^{-1}$ . (b) Chronoamperometric measurement for 24 hours at an applied voltage of  $1.0 \text{ V}$ .

power sources, the rate at which H<sub>2</sub> and O<sub>2</sub> are produced may in fact be quite slow. Therefore, solar electricity stations can be directly used to drive the electrolysis in base-acid hybrid electrolytic cell, because their low power output can match the limited Li-ion diffusion rate across the ceramic LATSP film. On the other hand, the Li-ion diffusion across the ceramic LATSP film lead to additional energy consumption, which is the inherent disadvantage of the base-acid hybrid water electrolysis cell. More and more efforts are being made to increase the conductive of ceramic electrolyte (i.e. lithium-ion conductive film), and thus it could be expected that electrolysis rate of base-acid hybrid electrolytic system could be improved step by step. In addition, the lower driving voltage for electrolysis may increase the utilization of solar energy. It is well known that solar energy can only be exploited when it's bright and daytime. The cloudy skies or sunshine at every dawn/evenfall much reduces the output voltage of solar cell. Herein, we take a commercialized solar cell (see supplementary Fig. S7) as an example to clarify this point. It can be detected that this cell exhibits a voltage of around 2.0 V at noon, but the cell voltage reduces to around 1.0 V at afternoon (see supplementary Fig. S8). In other words, for this cell, only several hours of the daytime can be efficiently employed for conventional water electrolysis that generally needs a driving voltage of 1.8 to 2.0 V. However, for the base-acid hybrid electrolytic cell, the output voltage of 1.0 V still can be used to produce H<sub>2</sub> and O<sub>2</sub> (Fig. 4).

Owing to the anodic reaction ( $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$ ) and the cathodic reaction ( $4\text{H}^+ \rightarrow 2\text{H}_2 - 4\text{e}^-$ ), this base-acid hybrid electrolytic system should consume OH<sup>-</sup> and H<sup>+</sup> during O<sub>2</sub> and H<sub>2</sub> production. However, acid/base production has been maturely developed. Especially, waste acid and base are serious environment issue due to their wide application in current chemistry industry. Currently, waste acid (or base) neutralization is the most common waste management practice globally. However, waste acid neutralization is yet to be used for any work/energy generation because of the low concentrations of the waste acid and the high heat capacity of aqueous solutions.<sup>43</sup> The basic-acidic hybrid electrolyser mentioned above can employ waste acid and base to produce H<sub>2</sub> and O<sub>2</sub> (see Fig. 4; in this experiment, the waste acid

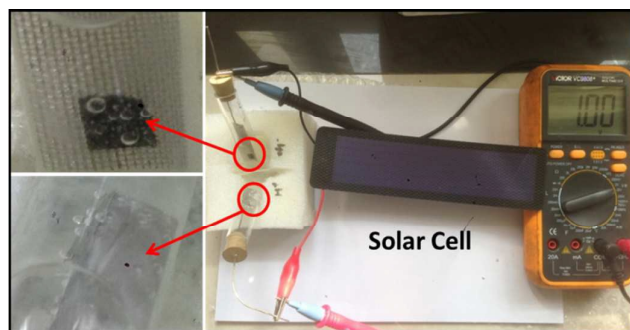


Fig. 4 Solar cell derived base-acid hybrid electrolytic cell. In this experiment, the waste acid and base from our lab were used as electrolytes for HER and OER. The solar cell was operated in the room without radiation of sunshine directly, and thus exhibited low output voltage of around 1.0 V. Even at such low voltage, H<sub>2</sub>/O<sub>2</sub> bubbles still can be detected on Pt-foil electrode and CoO-nanowire-electrode.

and base from our lab were used as electrolytes for HER and OER), and potentially provides a new approach for acid/base management. However, it should be noted that present case is just an initial proof-of-concept study. In practical application, the use of waste acid and waste base still faces great challenges, such as the transportation and handling of waste acid/base and their poisoning effects on catalyst. These issues should be further investigated in future research.

For conventional water electrolytic system that is based on acidic or basic electrolyte solution, the HER and OER are separated by proton exchange membranes (e.g. Nafion film) or porous membranes<sup>12</sup>. With regard to obtaining a H<sub>2</sub> stream via water splitting that is essentially free of O<sub>2</sub> and of sufficient purity of use in industrial processor or in a fuel cell, systems in which O<sub>2</sub> and H<sub>2</sub> are created at separated points in space are currently essential. Unfortunately, the gas still can permeate these above membranes to result in generation of H<sub>2</sub>/O<sub>2</sub> mixture. As pointed out by recent report<sup>11</sup>, there are few general and scalable electrolytic systems that can separate the production H<sub>2</sub> and O<sub>2</sub> in time. In this base-acid hybrid electrolytic system, the H<sub>2</sub> and O<sub>2</sub> are totally separated by a ceramic lithium-ion conductive glass film that can efficiently prevent gas permeating.

In summary, a base-acid hybrid electrolytic system, in which OER in a basic solution containing Li-ion and HER in an acidic solution are separated by a ceramic Li-ion exchange membrane, has been developed. Its operation depends on OER in basic electrolyte solution and HER in acidic electrolyte solution, accompanied by Li-ion diffusion from basic electrolyte solution to acidic electrolyte solution. This architecture benefits from the low OER potential in basic electrolyte solution and the high HER potential in acidic electrolyte solution, exhibiting a low driving voltage less than 1.23 V. It is demonstrated that the reduced driving voltage can increase the utilization of solar energy for H<sub>2</sub>/O<sub>2</sub> production. The H<sup>+</sup>/OH<sup>-</sup> computation characteristic may provide a promising approach for waste acid/base management. Finally, the ceramic (or glass) separator efficiently gets rid of the issue of gas crossover.

The authors acknowledge funding support from the Natural Science Foundation of China (21333002), Shanghai Pujiang Program (13PJ1400800), and Shanghai Science & Technology Committee (08DZ2270500).

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