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Supplementary information

Properties and composition of the spent electrolyte for premium circulation mediated by Al-air battery

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Supporting Experimental Details

Ionic conductivity:

The ionic conductivity of different spent electrolyte was calculated through the following equation:

$$\sigma = d / (A \times Rs) \quad (1)$$

where d is the distance (1.50 cm) between the two platinum foil electrodes, A represnets the area (1 cm^2) of the platinum foil electrode, and Rs means the resistance (ohm) of the electrolyte (obtained from EIS).

Causticity (α_k):

The α_k of different spent electrolyte were calculated through the following equation:

$$\alpha_k = 1.645 \times c(Na_2O) / c(Al_2O_3) \quad (2)$$

where $c(Na_2O)$ and $c(Al_2O_3)$ mean the concentration of Na_2O and Al_2O_3, respectively.

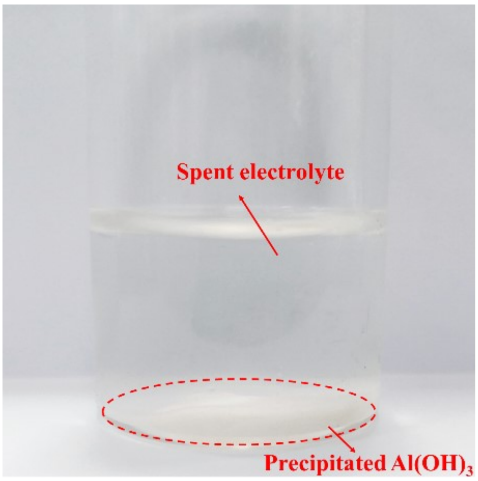

Fig. S1 The spent electrolyte after discharging at 75 mA cm^{-2} for 8 h with a temperature 25 ℃

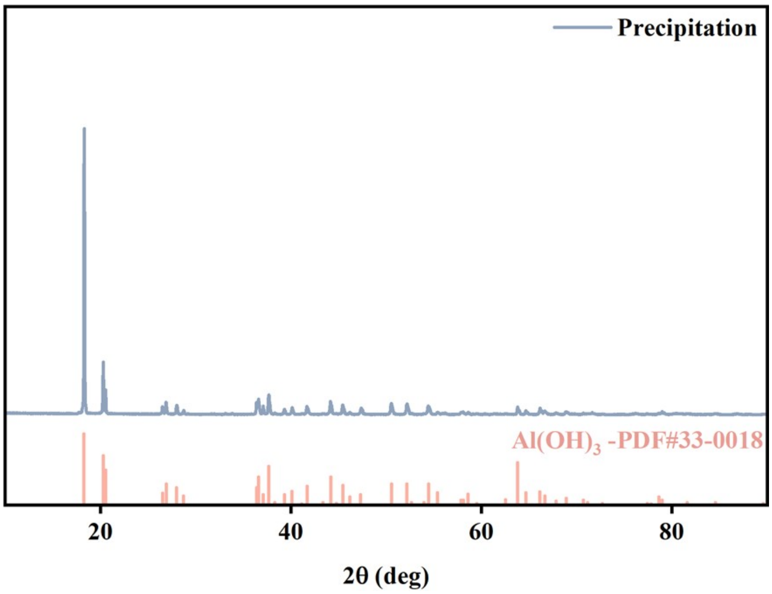

Fig. S2 XRD pattern of the precipitation

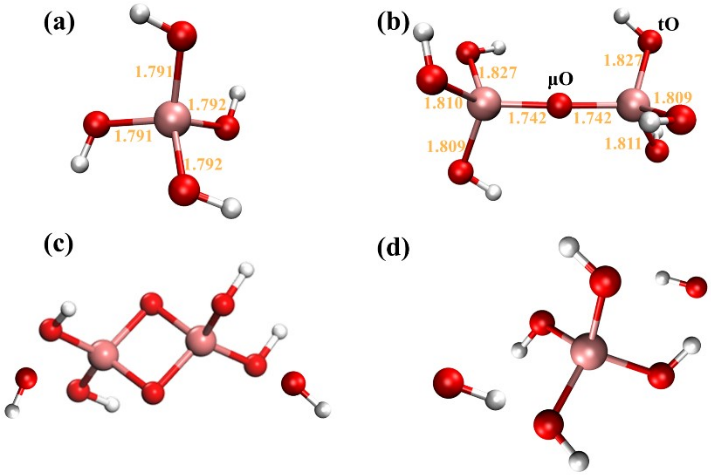

Fig. S3 The structures of aluminate ions were optimized in vacuum: (a) $Al(OH)_4^-$; (b) $[Al_2O(OH)_6]^{2-}$; (c) $[Al_2O_2(OH)_6]^{4-}$; (d) $Al(OH)_6^{3-}$

Supplementary Note 1: The explanation of the cycling fuel efficiency of AABs

Al-air batteries (AABs) have the potential to produce power to operate and other vehicles. Fascinatingly, the reaction product of the AABs could also be recycled. The product of the discharge reaction is $NaAl(OH)_4$ which is precipitated in the form of hydrargillite, $Al_2O_3 \cdot 3H_2O$ or $Al(OH)_3$. This could be heated and decomposed into Al_2O_3. The Al_2O_3 is regenerated to aluminum metal by electrolysis. Then, the aluminum metal is further placed in the battery. A cycle loop is finally established for aluminum. During the cycling, there are four components of the fuel cycle energy balance, including the usable energy contained in the aluminum anode, the heat of reaction from $Al(OH)_3$ to Al_2O_3, the heat of reaction from Al_2O_3 to Al, and unused aluminum reformed to anode plates. The above four components of energy are unified into the actual total energy (E_{total}) required for recycling. And energy efficiency (μ_1) for regeneration and recycle (E_{pro}/ E_{total}) is the energy produced from the battery (E_{pro}) divided by the energy required for recycle. Meanwhile, a battery efficiency (μ_2) and motor/transmission efficiency (μ_3) results in the EVs operating efficiency. Finally, these factors lead to a total cycling fuel efficiency of AABs ($\mu = \mu_1 \times \mu_2 \times \mu_3$) for the Al/air EVs. Specifically, the calculation of cycling fuel efficiency is calculated based on the 1 mol of aluminum.

Supplementary Note 2: The detailed statement for the aluminum resource cyclic process about Figure 1

Figure 1 illustrates the cyclic process for aluminum resource mediated by AABs. And the yellow arrows bound by two dashed lines means the circulation orientation for aluminum resource in the Figure 1. AABs system possess a high and attractive theoretical voltage, energy density, low cost, an environmentally benign and recyclable product. It would be a promising alternative to provide power to the vehicles. Importantly, AABs are primary batteries, which could not be charged. Aluminum anode continuously dissolves into the electrolyte during the discharging, resulting in the spent alkaline Al-containing electrolyte which is also called aluminate solution. It would degrade the battery performance. Regular replacements of the electrolyte are executed to ensure the normal operation of the battery. Therefore, a station should be set for replacement and storge of spent electrolyte, which is coined the electrolyte unit in Figure 1. With the accumulation of spent electrolyte, it is very necessary to dispose. Aluminate solution is an important mixture for manufacturing different aluminum products, such as fire retardant ($Al(OH)_3$) and burnishing powder (Al_2O_3). Furthermore, aluminum metal and alloy could be reproduced in electrolysis cells based on Hall-Héroult process. It is a very mature process chain for aluminum industry. Finally, the secondary aluminum metal and its alloy could be used in the AABs again. Therefore, an obvious and efficient cycling could be achieved for aluminum resources.

The current problem of this process mostly concentrates on the application of the AABs. Aluminum is oxyphilic, resulting in a compact protective layer on the aluminum surface. It would lead a terrible polarization in the neutral solution. Considering the recycling process, alkaline solution is adopted to remove the Al_2O_3 protective layer. Subsequently, a serious hydrogen evolution corrosion occurs to the alkaline system. It would decrease the voltage and utilization ratio of the aluminum anode, leading a dreadful battery performance. An obvious gap between the theoretical and practical energy density. Therefore, it is urgent to solve the problem of hydrogen evolution corrosion. Based on this, it has been also proposed many methods to address the problem, such as applying the aluminum alloy, or adding the corrosion inhibitors, H-bond trapping agent and molecule crowd agent into the electrolyte. Furthermore, researches have mainly focused on improving the battery performance. The insight into the spent electrolyte is still vague. Thence, it is significant to analyze the characteristics and composition of spent electrolyte under different discharge conditions.

Supplementary Note 3: The relationship between aluminate structures and the crystallization of $Al(OH)_3$

Aluminum is amphoteric. It could react with alkaline solution and generate unstable aluminate ions. Extremely complex and diverse aluminate species exist in the solution. Then, aluminum hydroxide would precipitate with the chemical reaction among the different aluminate ions, which is different from the general crystallization process. It is an important step for the Bayer process to obtain aluminum hydroxide in the aluminum electrolysis industry. Aluminate ions in the form of $Al(OH)_4^-$ are pervasive and main structure in the alkaline solution. However, it cannot be the basic unit of aluminum hydroxide precipitation owing to the stronger coordination ability and coordination trend of $Al(OH)_4^-$. As the advances of research, it is popularly regarded that $Al\text{-}(OH)_6$ with octahedral structure is the basic structure unit for growth. $[Al(OH)_4(H_2O)_2]^-$ is the minimum unit for growth. And $[Al_6(OH)_{18}(H_2O)_6]$ is a favorable unit for the precipitation of aluminum hydroxide, which is beneficial to the continuous condensation of basic structure and the formation of crystal nucleus. During the initial prenucleation stage, aluminate monomer would convert to the dimer aluminate and then transformed into trimer, tetramer and higher poly-aluminate. Principally, these structures differ from each other for only a few hydrogen atoms and water molecules. Subsequently, all forms of the precipitated $Al(OH)_3$ consist of octahedrally coordinated aluminums connected by bridging hydroxide ions in a layered structure of six-membered rings (the symbol $Al(OH)_3$ represents the amorphous, pseudo, boehmite, bayerite and gibbsite series). Thence, the structures of aluminate ions show a significant effect on the process of the crystallization for different $Al(OH)_3$ types.

Supplementary Note 4: The effect of causticity ratio on the aluminate structures

Causticity ratio is the molar ratio of Na_2O and Al_2O_3 in sodium aluminate solution, which directly reflects the saturation degree of alumina and the stability of the solution. And it means the relative amount of Na_2O and Al_2O_3. In our research, the amount of Na_2O showed slight change. And the Al(III) comes into the spent electrolyte during the discharging, resulting in the upshift amount of Al_2O_3. Correspondingly, causticity ratio manifests a decrease trend. The lower the causticity ratio, the higher the saturation degree. A consensus shows that $Al(OH)_4^-$ is the main ion structure under the different conditions. When the temperature and other factors are determined, $Al(OH)_4^-$ would polymerize to the ions bridged with Al-O-Al as the causticity ratio decreases. There may also be some $Al(OH)_5^{2-}$ and $Al(OH)_6^{3-}$. The interactions among the aluminate ions, Al(III), OH^- and H_2O would enhance with the upshift of the Al(III) concentration. However, the structure and stability of aluminate ions even is connected with methods of preparation, storage time and et al. A difference would observe at the different aluminate solution systems. Additionally, the causticity ratio needs to be strictly controlled to maintain the saturation degree in the actual production process of aluminum hydroxide. It could promote the precipitation rates of aluminum hydroxide.