Low-Temperature Performance of Al-air Batteries

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Abstract: High demand for batteries with a wide operating temperature range is on the rise with the development of wearable electronic devices, especially electric vehicles used in cold regions. Al–air batteries for electric vehicles have triggered worldwide interest due to their excellent theoretical energy density and safety. In this study, the low-temperature performance of Al–air batteries is tested for the first time. The effects of temperature and electrolyte concentrations on the discharge performance are then studied in detail. The discharge voltage is significantly influenced by the temperature. The low temperature could significantly depress the hydrogen evolution reaction of Al anodes. The Al–air batteries reached an extraordinary capacity of 2480 mAh/g, with 31 wt% KOH electrolyte at −15 °C. Moreover, the Al–air batteries at 0 °C exhibited higher discharge voltage and power densities than those at 15 and −15 °C. This study provides an important reference for future studies to improve low-temperature performance of Al–air batteries.

Keywords: al-air battery; low temperature; discharge performance

1. Introduction

Besides the rapid advancement of modern industrial technology, other factors, such as environment friendliness, cleanliness, and being an alternative inexpensive energy source have become the subject of research because of the limitations of traditional energy, i.e., fossil fuel exhaustion and risk of climatic degeneration [1]. Metal–air batteries are one of the most promising candidates for next-generation energy storage due to their high capacity and energy density. Al–air batteries have driven the increasing concern due to their high specific energy density, low cost [2], and stability in solid gel electrolyte [3] or the electrolyte with additives (such as ZnO/PEG di-acid inhibitor and non-conductive oil) [4,5]. The application of these batteries has spread to remote communications, railroad signaling, seismic telemetry, and power grids. Moreover, the high safety and long platform of discharge make them a prominent power storage source for hybrid electric vehicles [6,7]. Although significant progress has been achieved in enhancing the electrochemical performance of Al–air battery, a critical issue that seriously restricts its future commercialization and practical application remains. Batteries are sensitive to environmental conditions, especially to temperature. However, few studies focus on low-temperature (LT) performance of Al–air batteries, which is of considerable importance for the development of Al–air battery. For example, understanding the effects of winter operation for electric vehicles is critical in cold regions, such as Switzerland, Canada, Northern USA, Northeast China, and Russia.

Scientists have already realized that a broad application temperature range is a big challenge for battery development. Numerous papers have addressed the problem of poor LT performance of
various kinds of batteries [8–13]. If the temperature falls to the subzero range, then the electrochemical performance and stability of batteries can be dramatically reduced, depending on the battery chemistry in comparison with those at room temperature. Ji et al. [14] have shown that the sluggish diffusion process of ions at LT leads to the remarkable deterioration of electrochemical performance. For vanadium redox flow batteries, a relatively low energy density is limited by the solubility of vanadium ions in the sulfuric acid supporting electrolyte at LT [15]. The high capability and cycling stability of Na-ion batteries are substantially reduced when temperature falls below 0 °C [16]. Most studies focused on the LT performance of Li-ion batteries, particularly for propelling electric vehicles [11,17–19]. Some studies suggest that discharge capacity and operating voltage are limited by the poor ionic conductivity of electrolytes and low diffusivity of lithium ion within graphite anodes at LT. A study reported that Li-ion batteries could only deliver 5% of its capacity at −40 °C compared with that at 20 °C [12,20]. Researchers focus on improving battery cycling stability and capacity at LT [14,21–28]. Al–air batteries exhibit evident advantages over Li-ion batteries. Al–air batteries are safe and cost effective, and their raw materials are widely available. These advantages demonstrate that the Al–air battery has the potential to be a backbone technology for the energy storage of electric vehicles in the future. However, the LT performance of the Al–air battery has never been tested or investigated. Therefore, studying the mechanisms of LT performance for the Al–air battery is crucial and challenging.

Based on the aforementioned reasons, the LT electrochemical performance for Al–air batteries is comprehensively tested in this study. The following section presents a detailed fabrication of the Al–air battery. In addition, the electrochemical performance is tested and discussed. The results could provide suggestions for developing better-performing Al–air batteries.

2. Experiment

2.1. Materials

All materials in this study were of analytical grade and used without further treatment. Reagents for the air cathode synthesis, including activated carbon, ether black, poly(vinylidene fluoride) (PVDF), and Ni foam, were purchased from Shenyang Kejing. Catalysts, including MnO$_2$, La$_2$O$_3$, SrO, and ZnO, were from Sinopharm Chemical Reagent. Organic solvent N-methyl pyrrolidone (NMP) was provided by Shanghai Hushi Laboratorial Equipment Co., Ltd. Al foil and KOH (from Chinasun Specialty Products Co., Ltd.) solution served as the metal anode and electrolyte, respectively.

2.2. Fabrication of Al-air Batteries

Air cathode was prepared according to the method used in our previous study [3], with conductive carbon materials, catalysts, binder, and current collector. A mixture of activated carbon (70 g), ether black (10 g), MnO$_2$ (10 g), La$_2$O$_3$ (8 g), and SrO (2 g) was milled together with PVDF (8 g) binder. Thereafter, the solid blend in NMP dispersed, forming a 400 ml viscous paste, which was smeared evenly on the surface of the Ni foam and dried for 24 h at ambient temperature. A 0.3 mm-thick cathode plate was obtained by pressing it at 8 MPa.

All experiments comprised KOH and ZnO aqueous alkaline solutions in distilled water as an electrolyte. ZnO additive in alkaline solutions was used as a corrosion inhibitor [3,5,29–33]. The concentrations of KOH and ZnO were $\alpha$ and $(\alpha/30)$ wt% respectively. Al foil with 20 μm thickness was used as the metal anode and cut into 6 cm × 6 cm, and the reaction area is a circle with a diameter of 4 cm and weight of 0.067 g. The Al–air batteries were finally assembled, as shown in Figure 1. The distance between the aluminum and air electrode is 6 cm.
2.3. Electrochemical Tests

Conductivity is one of the most important factors that affect electrochemical performance. Different contents of KOH pellets were added into distilled water, and the conductivities were measured each time at different temperatures. A pair of Pt electrode was immersed in the electrolyte solution to measure the conductivity with a Mettler Toledo FE30 conductivity testing system. Discharge characteristics of the assembled Al-air batteries were measured using a LAND battery testing system at room, zero, and subzero temperatures. Once the cell was assembled, a 5 min period was left to allow good impregnation of electrodes to stabilize the open circuit potential. To characterize the self-discharge behavior, Tafel extrapolation was performed using an electrochemical workstation RST5000 in the conventional three-electrode cell. A Platinum wire was used as the counter electrode and mercury/mercuric oxide (Hg/HgO) was used as the reference electrode. The working electrode was the Al anode. After the Al anodes were immersed in electrolyte for 20 min to allow for potential stabilization; potentiodynamic polarization was conducted at a 1 mV/s scan rate. The voltage scan range of the anodic polarizing curve was −0.5 to 0.5 V vs. open circuit potential.

3. Results and Discussion

3.1. Ionic Conductivity

Figure 2 shows the conditions of KOH solution (with α = 20, 30, and 40 concentration), which was kept frozen for 24 h at −25 °C. Distilled water was also frozen for comparative purposes. As shown in the figure, the KOH solution at a low concentration (20 wt%) was frozen, and the solution still flowed evenly at extremely LT at high concentrations. This finding illustrates well that KOH solution with concentration higher than 20 wt% could be adopted in Al–air battery at LT.

Figure 3 displays the conductivity of electrolyte solution (including KOH and ZnO) in terms of the mass fraction of KOH and temperature. The conductivity decreases further with decreasing temperature. Conductivity decreases with increasing KOH content after the peak because of increased viscosity and restricted ion mobility [34–36]. The highest conductivity of around 560 mS cm⁻¹ is observed at KOH content 31.5 at 15 °C. Fairly high conductivity of 230 mS cm⁻¹ with content 28 wt% is evident when the temperature is lowered to −15°C. The KOH content is fixed at 25 and 31 wt% (α = 25 and 31) in the following research.
Figure 2. Photographs of KOH at different concentrations after being frozen for 24 h at −25 °C. Pure water on the left is used for comparison.

Figure 3. Conductivity curve of KOH at different concentrations and temperatures.

3.2. Electrochemical Characterization

Figure 4 shows the discharge behaviors of the Al–air battery using 25 wt% KOH electrolyte solution at constant current densities of 0.5 mA cm\(^{-2}\) (a) and 1.0 mA cm\(^{-2}\) (b). The result shows that the Al–air battery at 0 °C exhibits an open-circuit voltage of 1.41 V, which is higher than that of other temperatures, whereas the lowest open-circuit and platform voltage appeared at −15 °C. The cathode reaction would be affected by the diffusion coefficient of oxygen. According to Arrhenius-type equation [37], the gas diffusion coefficient decreases with temperature. However, proper LT would inhibit the hydrogen evolution of Al anode. Additionally, the discharge time of the Al–air battery at −15 °C is unexpectedly up to 25 h. The discharge time is related to the utilization of Al foil. The hydrogen generation was barely observed at −15 °C, thereby indicating that the LT improves the stability of the Al–air battery and suppresses the parasitic reaction. At a discharge current density of 0.5 mA cm\(^{-2}\) (Figure 4a), the Al–air battery achieves a capacity of 116 mAh/g at 25 °C, which is only 4.03% of aluminum’s theoretical capacity (2980 mAh/g [38]), and the gravimetric energy density is 142 Wh/g. At −15 °C, Al–air battery exhibited a much superior capacity of 2343 mAh/g at the same current density, which is 78.68% of the theoretical value. The gravimetric energy density is 2480 Wh g\(^{-1}\). Compared with the current density 0.5 mA cm\(^{-2}\) case, the capacity increases by 1.12, 1.84, and 2.175 folds at −15 °C, 0 °C, and 15 °C, respectively, at 1.0 mA cm\(^{-2}\) (Figure 4b). The conductivity of electrolyte is essential for the discharge performance. LT results in the reduction OH\(^{−}\) activity, which also improves the oxygen reduction reactions. The extraordinary capacity is mainly due to the effect of LT on the anodic reaction.
Figure 4. Discharging voltage profiles with a constant current density of 0.5 mA cm\(^{-2}\): (a) and 1.0 mA cm\(^{-2}\); (b) by using 25 wt% KOH.

The discharging performances are also tested using a higher concentration (31 wt%) KOH electrolyte solution with constant current densities of 0.5 and 1.0 mA cm\(^{-2}\). With increasing electrolyte concentration, the Al–air battery achieves high discharge voltage but low capacities, as shown in Figure 5. When the electrolyte concentration is high, the aluminum oxidation rate increases. Therefore, the batteries exhibit high discharge voltage, short discharge time, and low capacities.

Figure 5. Cont.
The potentiodynamic polarization at different temperatures was measured using a three-electrode system. Figure 6 and Table 1 respectively present the Tafel curves and corresponding corrosion parameters of Al anodes in 25 wt% KOH (Figure 6a) and 31 wt% KOH (Figure 6b) electrolyte solutions. The values of the corrosion potential ($E_{corr}$) and the corrosion current density ($I_{corr}$) are calculated from the Tafel plots. The corrosion inhibition efficiency is calculated by the following formula as used in Reference [39–41].

$$\eta\% = \frac{I_{corr} - I_{corr inh}}{I_{corr}} \times 100,$$

where the $I_{corr}$ and $I_{corr inh}$ are the corrosion current densities at 15 °C and other temperatures, respectively. Based on the Tafel plot results, the corrosion current density of Al–air batteries at 15°C is clearly much larger than that of 0 or −15 °C, and the corrosion potential shifts, implying that it is less corrosion resistant and possesses the largest self-corrosion rate than that of others. As illustrated in Table 1, the inhibition efficiencies are much high at LT. The largest inhibition efficiency is obtained at −15 °C. This finding further confirms the discharged behaviors in Figures 4 and 5. The LT can significantly prevent the corrosion of aluminum anodes in KOH electrolyte solution.

**Figure 5.** Discharging voltage profiles with a constant current density of 0.5 mA cm$^{-2}$; (a) and 1.0 mA cm$^{-2}$; (b) by using 31 wt% KOH.

**Figure 6.** Cont.
potentials and power densities increase, as plotted in Figure 7b. The maximum power densities reach 104 ± 2.9 mW cm⁻² (0 °C) at 130 mA cm⁻², which is more than 95.55 ± 2.7 mW cm⁻² (15 °C) and 84.37 ± 2.6 mW cm⁻² (−15 °C). These data provide rather surprising results, thereby suggesting that the proper LT improves the power density of Al–air battery. Although the LT environment lowered the electrical conductivity of electrolyte solution, LT repressed the hydrogen evolution reaction and promoted oxygen reduction reactions to a certain degree.
Figure 7. Discharging voltage and power density profiles versus current density with 25 wt%: (a) and 31 wt%; (b) KOH electrolyte solutions.

4. Conclusions

Measurements for LT electrochemical performance of Al–air batteries are reported for the first time. The combination effects of temperature and electrolyte concentrations on electrochemical performance are discussed. Different temperatures are included for comparison. The LT has a significant effect on the discharge performance. In the tests of constant current discharge, the capacities of Al–air batteries can reach 2343 mAh/g with 25 wt% KOH electrolyte and 2480 mAh/g with 31 wt% KOH electrolyte at −15 °C. The corrosion experiments of Al anodes further demonstrate that the LT could effectively decrease the hydrogen evolution reaction. Surprisingly, the Al–air batteries at 0 °C exhibit high discharge voltage and power densities. The peak value of power densities at 0 °C reaches 101.14 ± 2.8 mW cm⁻² (25 wt% KOH) and 104 ± 2.9 mW cm⁻² (31 wt% KOH) at 130 mA cm⁻², which is higher than that of −15 °C and 15 °C. Therefore, the proper LT could improve the performance of Al–air batteries. This novel result is crucial to studies focusing on power sources for wide temperature ranges. Further studies on the improvement of LT of metal–air battery are needed.

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References


16. Lee, M.J.; Lho, E.; Bai, P.; Chae, S.; Li, J.; Cho, J. Low-temperature carbon coating of nanosized Li1.015Al0.985O4 and high-density electrode for high-power Li-Ion batteries. *Nano Lett.* **2017**, *17*, 3744–3751. [CrossRef] [PubMed]


Liu, J.; Lin, X.; Han, T.; Li, X.; Gu, C.; Li, J. A novel litchi-like LiFePO4 sphere/reduced graphene oxide composite Li-ion battery cathode with high capacity, good rate-performance and low-temperature property. *Appl. Surf. Sci.* 2018, 459, 233–241. [CrossRef]

Tripathy, Y.; McGordon, A.; Low, C. A New Consideration for Validating Battery Performance at Low Ambient Temperatures. *Energies* 2018, 11, 2439. [CrossRef]


Inoishi, A.; Nishio, A.; Yoshioka, Y.; Kitajou, A.; Okada, S. A single-phase all-solid-state lithium battery based on Li1.5Cr0.5Ti1.5(PO4)3 for high rate capability and low temperature operation. *Chem. Commun.* 2018, 54, 3178–3181. [CrossRef] [PubMed]


Kang, Q.X.; Wang, Y.; Zhang, X.Y. Experimental and theoretical investigation on calcium oxide and L-aspartic as an effective hybrid inhibitor for aluminum-air batteries. *J. Alloys Compd.* 2019, 774, 1069–1080. [CrossRef]