

10th International Conference on Applied Energy (ICAE2018), 22-25 August 2018, Hong Kong, China

Low-cost Al-air batteries with paper-based solid electrolyte

Yifei Wang^{a*}, Wending Pan^a, Holly Kwok^a, Xu Lu^b, Dennis Y.C. Leung^{a*}

^aDepartment of Mechanical Engineering, the University of Hong Kong, Hong Kong, China

^bDepartment of Chemistry, Yale University, New Haven, Connecticut 06520, United States

Abstract

This work demonstrates a novel-type paper-based solid electrolyte (PBSE) and its application in Al-air battery, which is targeted for miniwatt applications. Benefited from the solid-form electrolyte, a liquid-free operation of the Al-air battery is realized, eliminating the potential leakage hazard and therefore improving the battery practicability. The PBSE is prepared by impregnating gel electrolyte into porous cellulose paper, followed by a solution casting process to solidify the gel. The as-prepared PBSE can either be used in mechanical rechargeable Al-air batteries, or be integrated into single-use flexible Al-air batteries. Currently the PBSE can achieve a moderate battery performance with a peak power density of 3.8 mW cm⁻² and an Al specific capacity of 900.8 mA h g⁻¹. Properties of the PBSE can be further improved by a comprehensive parametric study on its fabrication parameters, such as gel concentration, casting temperature, casting time, porosity and pore size of paper substrate, etc.

© 2019 The Authors. Published by Elsevier Ltd.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

Peer-review under responsibility of the scientific committee of ICAE2018 – The 10th International Conference on Applied Energy.

Keywords: Paper-based; solid electrolyte; gel electrolyte; Al-air battery; miniwatt applications

1. Introduction

Since its first appearance in 1960s [1], Al-air battery has been regarded as a promising primary energy technology, which is mainly because of the low price, great abundance, less pollution and high energy density of Al. Like most metal-air batteries, Al-air battery generally employs an Al plate as anode, a gas diffusion electrode as cathode, and a strong alkaline solution as electrolyte. During battery operation, the Al anode is continuously

* Corresponding author. Tel.: (852) 3917 7911; fax: (852) 2858 5415.

E-mail address: yicleung@hku.hk

oxidized to generate free electrons, which flow through the external circuit to the cathode side. At the cathode, oxygen from the ambient air will be reduced and combined with the incoming electrons. Hydroxyl ions from the electrolyte are transported from the cathode to the anode, completing the whole charge circuit. Despite its high performance, currently this technology is greatly haunted by a notorious problem called the Al self-corrosion, which is mainly due to the high reactivity of Al in alkaline environment. In addition, other issues such as high cost of pure Al anode, complex water management and potential leakage hazard have also restricted the practical application of this technology. This is especially the case for miniwatt devices, which generally require simple-structure, lightweight and leakage-free power supply.

Recently, a novel type of solid-form electrolyte has been developed for Al-air batteries. This solid electrolyte is fabricated by adding water-absorbing polymers into alkaline solution, resulting in a semisolid gel electrolyte. In this manner, the water management sub-system such as pumping, tubing and electrolyte storage can be totally eliminated, leading to a greatly-simplified battery structure. Moreover, there is no leakage problem with the solid electrolyte, so that the battery safety level is greatly improved. Wu et al. [2] developed a polymer electrolyte membrane using poly(vinyl alcohol) and poly(acrylic acid) (PAA) for Al-air battery. The peak power density was relatively low (1.2 mW cm^{-2}), which is probably due to the low conductivity of its deactivated Al electrode surface. Mohamad [3] used hydroponics gelling agent to solidify KOH solution. With this solid electrolyte, the Al-air battery could achieve a peak power density of 5.5 mW cm^{-2} . Zhang et al. [4] employed PAA as gelling agent and ZnO as corrosion inhibitor into KOH electrolyte. Their all-solid state Al-air battery could obtain a very high power output of 91.1 mW cm^{-2} . Pino et al. [5] also tried PAA as gelling agent and explored the feasibility of commercial Al alloys as battery anode. In addition to PAA, other gelling agents such as xanthan and k-carrageenan were also investigated by Palma et al. [6]. Despite these achievements, the existing solid electrolytes in literature are generally bulky and rigid, which is neither convenient to use nor available for developing lightweight and flexible Al-air batteries.

Cellulose paper has been widely utilized for fabricating various types of power sources [7]. Paper is low-cost, ubiquitous, renewable, lightweight and flexible, which is very advantageous as a novel substrate material. Not only the electrodes and current collector can be deposited onto paper surface, but also the electrolyte can be impregnated into its porous inside. Therefore, in this work we have proposed a novel paper-based solid electrolyte (PBSE) for Al-air batteries, which employs the cellulose network of paper as skeleton to store the gelled alkaline electrolyte. This PBSE not only enables the fabrication of a lightweight flexible Al-air battery, but also contributes to a high-efficiency stacking of the Al-air battery pack.

2. Experimental

2.1 Preparation and characterization of the PBSE

As shown in Fig. 1(a), a gel electrolyte was prepared first by dissolving 40 mg sodium polyacrylate powder (SPA, Macklin) in 2 mL of 10 M sodium hydroxide (NaOH, Sigma-Aldrich) solution. After sufficient stirring and storing for 24 hours, the final product was a transparent gel with high viscosity. Next, 100 μL of the gel electrolyte was deposited into the filter paper (No.1, Advantec) by a pipette. To strictly confine the deposition area ($1 \text{ cm} \times 1 \text{ cm}$), the filter paper was sandwiched between two annular Poly(methyl methacrylate) (PMMA) plates with high pressure, so that the deposited gel electrolyte could not access the pressed part of the paper. After the gel electrolyte was fully impregnated into paper, it was casted at 60°C for 1 h to evaporate the excess water inside the gel, in order to achieve the desired solid-state. The final product and the schematic diagram of the PBSE were also shown in Fig. 1(a).

After preparing the PBSE, its micro morphology and elementary composition were studied by a Scanning Electron Microscope (Hitachi 3400N) and an Energy Dispersive X-ray Detector (EDX). Its conductivity was also investigated by electrochemical impedance spectroscopy (EIS) analysis at 0 V, with a frequency range of 100 kHz to 0.1 Hz and an amplitude of 10 mV. To conduct the EIS test, two Pt foils were utilized to sandwich the PBSE with the help of PMMA shells.

2.2 Fabrication and testing of Al-air batteries with PBSE

2.2.1 The mechanical rechargeable Al-air battery with rigid shells

As shown in Fig. 1(b), the mechanical rechargeable Al-air battery was mainly composed of an Al foil anode (98.2% purity, kitchen foil), a carbon paper cathode (HCP120, Shanghai Hesun), and the PBSE sandwiched in between. Two PMMA shells were employed to assemble the three layers together with the help of four pairs of bolts & nuts. In addition, a $1 \text{ cm} \times 1 \text{ cm}$ window was cut out in the shell of the cathode side for air breathing. Ag foil was

connected to the carbon paper by Ag glue as the cathode current collector. As for the anode, the Al foil itself can be used for current collection.

2.2.2 The flexible Al-air battery and battery pack

To develop the flexible Al-air battery, the rigid carbon paper can no longer be used as cathode. Instead, an oxygen reduction reaction (ORR) ink was developed by dispersing 50 mg carbon nanotube (CNT, Aladdin) and 1.7 mg Nafion binder (DuPont) into 1 mL ethanol-water solution (1:1), followed by 30 minutes' sonification. The battery structure is shown in Fig. 1(c). An Ag grid (5 x 5, 1 cm² total area) was drawn on the filter paper first, followed by depositing 20 μ L of the as-prepared ORR ink onto it. After ink drying, the gel electrolyte was deposited into the filter paper from the other side, which was also dried at 60 °C for 1 h. Finally, a 1 cm x 1 cm Al foil was attached to the other side of the filter paper with the help of a double-conductive Cu tape, which also served as the anode current collector. In addition to this single cell, a 10-cell flexible Al-air battery pack was also developed in the same way, which was connected in series to improve its voltage output ability.

2.2.3 Battery testing and post-test characterization

Battery testing was conducted with the help of an electrochemical workstation (CHI660E). To obtain the battery polarization curve, the linear sweep voltammetry (LSV) technique was utilized from battery OCV to 0 V with a sweep rate of 5 mV s⁻¹. In addition, the battery discharge stability was studied by galvanostatic discharge test at 1 mA cm⁻², with 3.5 mg Al foil as anode. The corresponding Al specific capacity was also calculated based on the discharge result. Furthermore, for the mechanical rechargeable Al-air battery, the used PBSE after discharge test was taken out for further characterization. Its surface morphology and element composition were investigated by SEM and EDX, which were also compared with the fresh PBSE.

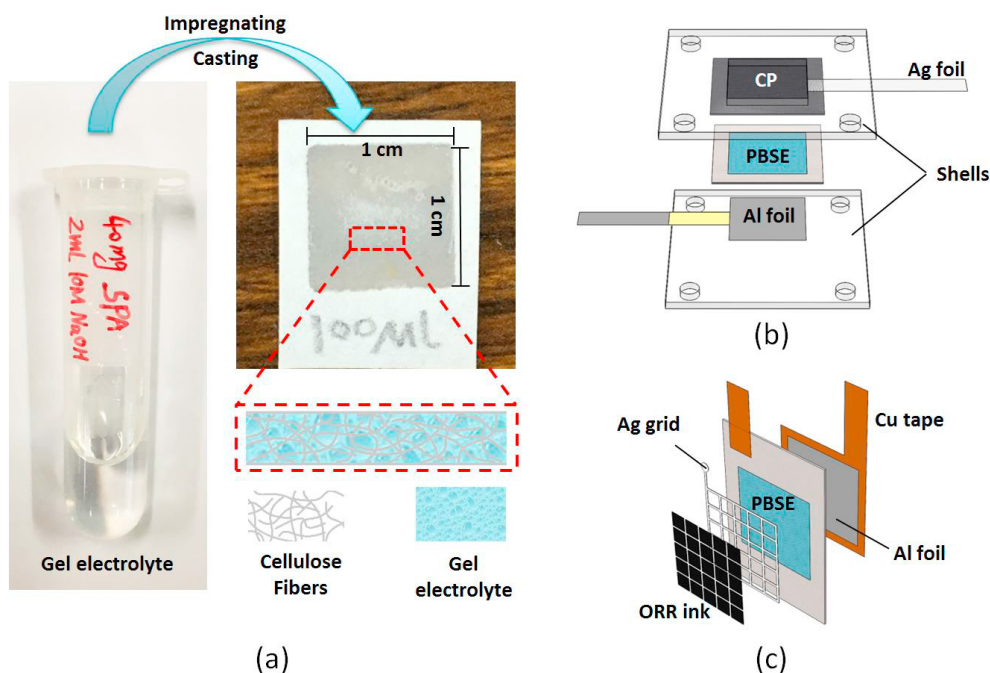


Fig. 1 PBSE for Al-air batteries: (a) Schematic diagram of the PBSE; (b) Composition of the mechanical rechargeable Al-air battery; (c) Composition of the flexible Al-air battery.

3. Result & Discussion

3.1 Physical characterization of the PBSE

Before electrochemical testing, surface morphology of the as-prepared PBSE was investigated first by SEM. As shown in Fig. 2(a), the pristine filter paper (upper image) was composed of multiple intertwined cellulose fibers.

After gel electrolyte deposition (lower image), the cellulose fibers and the pores between them were coated with the SPA-NaOH gel. However, some vacant pores could still be observed in the PBSE, indicating that the space inside paper was not totally filled by the gel electrolyte. This is probably because of the low-pressure environment of the SEM test (70 Pa), which promoted the further evaporation of water inside the gel. In the future, SEM test of less-dried PBSE will be conducted to compensate this vacuum effect. Fig. 2(b) summarizes the element composition of both the pristine filter paper and the PBSE. Since the formula of cellulose is $(C_6H_{10}O_5)_n$, the C-O ratio of 1.17:1 of the pristine paper is very reasonable. By adding SPA-NaOH gel, the Na element was introduced into the paper, and the C-O-Na ratio was about 2:5:3. Furthermore, Fig. 2(c) compares the ionic conductivity between the PBSE and a filter paper soaked with NaOH solution. Apparently, the PBSE encountered much higher resistance than the latter, which was mainly because of the low ion mobility inside the gel electrolyte.

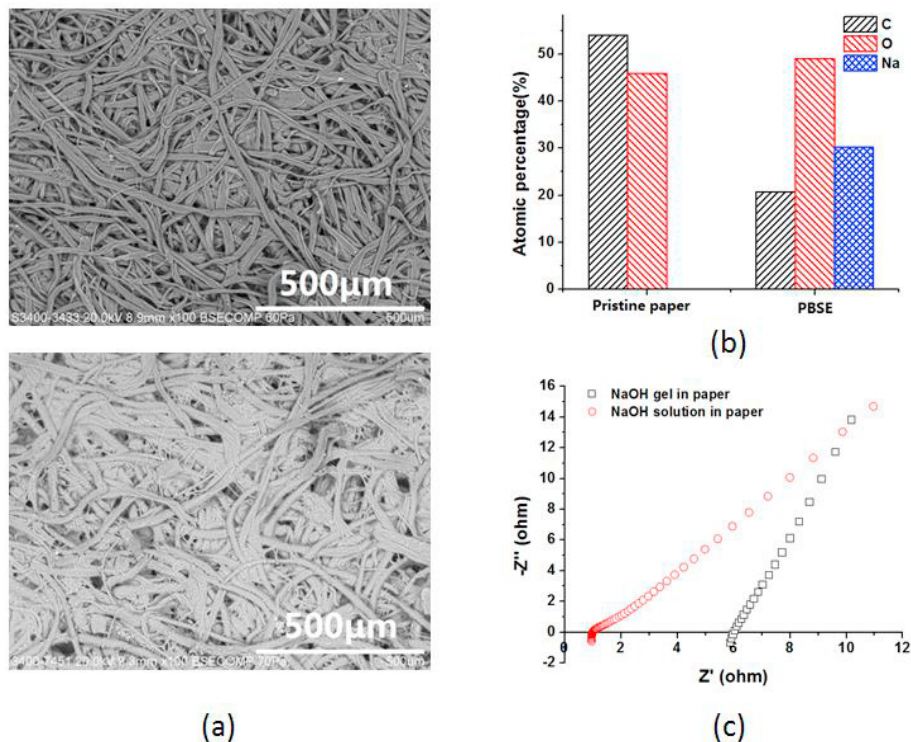


Fig. 2 Physical characterization of the PBSE compared with a pristine filter paper: (a) SEM image of the surface morphology; (b) Element composition by EDX; (c) EIS analysis of the ionic conductivity.

3.2 The mechanical rechargeable Al-air battery with PBSE

Al-air battery is generally not electrically rechargeable due to the fact that the Al electro-deposition is not thermodynamically feasible in aqueous electrolyte. Nevertheless, it can still be mechanically recharged by replacing the exhausted Al anode with a fresh one manually. This process is quite dangerous for conventional Al-air batteries because of the potential leakage of corrosive electrolyte. However, by utilizing the present PBSE, the mechanical recharge process would be very safe and convenient. Fig. 3(a) shows the cell performance of the mechanical rechargeable Al-air battery with PBSE. Currently, this cell could obtain an OCV of 1.5 V, a peak power density of 3.8 mW cm^{-2} and a maximum current density around 5 mA cm^{-2} . Compared with aqueous Al-air battery systems, the power and current output of this cell was limited. However, it is already sufficient for powering various miniwatt devices, which generally require mW or even μW level of power. In the future, the performance can be further improved by optimizing the PBSE itself or employing efficient ORR catalysts. Fig. 3(b) exhibits the galvanostatic discharge curve of the cell at 1 mA cm^{-2} . With only 3.5 mg Al foil, the present battery could discharge stably for 3 hours around 1.1 V, and the calculated Al specific capacity was as high as $900.8 \text{ mA h g}^{-1}$. After the discharge, it

was found that a large portion of the Al foil was not consumed but was separated from the anode current collector as shown by the inset, leading to a great waste of Al. This issue should be tackled in the future to further improve its discharge efficiency. After the discharge, the used PBSE was taken out to observe its surface morphology, which has slightly larger pores than the fresh PBSE. This is probably because of the consumption of water from the gel electrolyte during battery discharge. Furthermore, Fig. 3(d) demonstrates the element mapping of the used PBSE. Apparently, the anode reaction product, $\text{Al}(\text{OH})_3$, was left behind inside the used PBSE, which contained only these four elements. As a consequence, the used PBSE can be disposed freely without any environmental concerns.

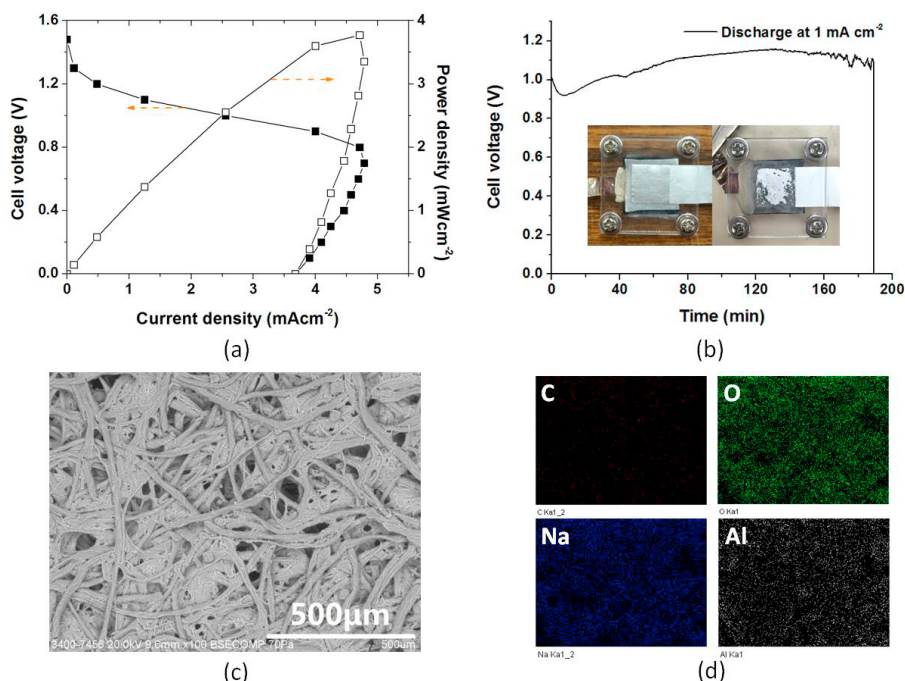


Fig.3 The mechanical rechargeable Al-air battery with PBSE: (a) Battery polarization curve; (b) Galvanostatic discharge at 1 mA cm^{-2} with 3.5mg Al as anode; (c) Surface morphology of the used PBSE after discharge; (d) Element mapping of the used PBSE after discharge.

3.3 The flexible Al-air battery and battery pack with PBSE

Compared with rigid batteries, flexible batteries can be utilized in more complicated and dynamic environment, such as for powering wearable devices on human body. Till now, different types of flexible power sources have already been developed, including both primary batteries and secondary batteries. The present PBSE is very promising for fabricating a solid-state flexible Al-air battery. As shown in Fig. 4(a), compared with the mechanical rechargeable battery with sufficient external pressure, the present flexible battery achieved slightly lower performance, with a peak power density of 2.4 mW cm^{-2} (37% lower). As shown in Fig. 4(b), when bended for 60° and discharged at 1 mA cm^{-2} , the flexible cell could also operate for 160 minutes, achieving a high Al specific capacity of 767.5 mA h g^{-1} . This result has demonstrated the good flexibility of this battery. Furthermore, the utilization of PBSE has also enabled the easy fabrication of a high-voltage, lightweight and flexible Al-air battery pack. As shown in Fig. 4(c), 10 single cells (3 mm x 3 mm electrode area) were fabricated within a single piece of filter paper with a size of 3.5 cm x 1.4 cm, and the total device weight was only 138 mg. This Al-air battery pack could generate an OCV as high as 13.2 V, which was mainly attributed to the total elimination of internal discharge among the single cells. On the contrary, when another battery pack without PBSE was provided with aqueous NaOH electrolyte, the ionic connection among the single cells would generate parasitic shunt currents inside the stack, leading to a poor OCV of only 1.6 V.

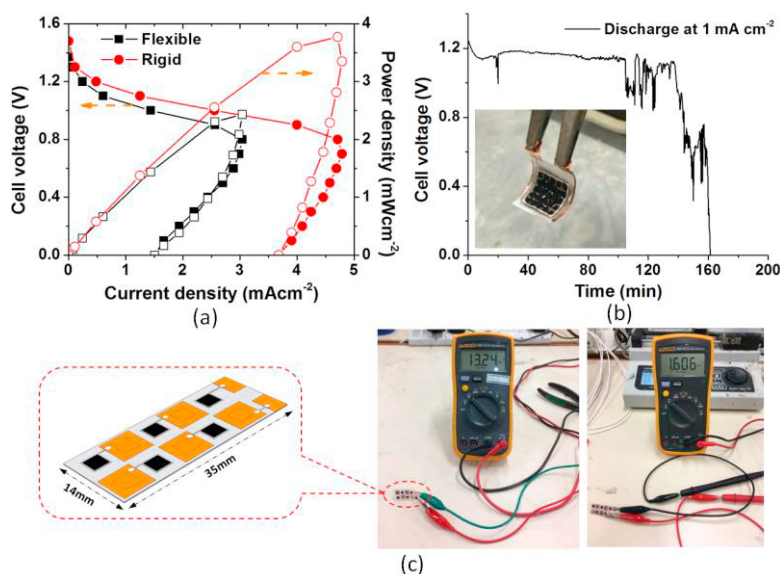


Fig. 4 The flexible Al-air battery and battery pack with PBSE: (a) Battery polarization curve; (b) Galvanostatic discharge at 1 mA cm^{-2} with 3.5 mg Al as anode; (c) A 10-cell battery pack connected in series.

4. Conclusion

In this work, a novel-type PBSE has been developed to facilitate the liquid-free operation of Al-air batteries for various miniwatt applications. The PBSE is fabricated by impregnating gel electrolyte into the cellulose network of paper, which can be conveniently applied to either mechanical rechargeable Al-air batteries or single-use flexible Al-air batteries. The mechanical rechargeable battery with PBSE can generate an OCV of 1.5 V and a peak power density of 3.8 mW cm^{-2} , which is sufficient for various miniwatt devices. The Al specific capacity is as high as $900.8 \text{ mA h g}^{-1}$. As for the flexible battery, currently its power output is slightly lower due to the insufficient contact between the battery components, which requires further improvement in the future. However, the utilization of PBSE enables the fabrication of a high-efficiency flexible battery pack with 10 cells connected in series. Without internal discharge, this micro Al-air battery pack can generate a high OCV of 13.2 V .

Acknowledgements

The authors would like to acknowledge the CRCG grant of the University of Hong Kong and the SZSTI of Shenzhen Municipal Government to provide funding support to this project.

References

- [1] S. Zaromb, The use and behavior of aluminum anodes in alkaline primary batteries, *Journal of The Electrochemical Society*, 109 (1962) 1125-1130.
- [2] G. Wu, S. Lin, C. Yang, Alkaline Zn-air and Al-air cells based on novel solid PVA/PAA polymer electrolyte membranes, *Journal of Membrane Science*, 280 (2006) 802-808.
- [3] A. Mohamad, Electrochemical properties of aluminum anodes in gel electrolyte-based aluminum-air batteries, *Corrosion Science*, 50 (2008) 3475-3479.
- [4] Z. Zhang, C. Zuo, Z. Liu, Y. Yu, Y. Zuo, Y. Song, All-solid-state Al-air batteries with polymer alkaline gel electrolyte, *Journal of Power Sources*, 251 (2014) 470-475.
- [5] M. Pino, J. Chacón, E. Fatás, P. Ocón, Performance of commercial aluminium alloys as anodes in gelled electrolyte aluminium-air batteries, *Journal of Power Sources*, 299 (2015) 195-201.
- [6] T. Di Palma, F. Migliardini, D. Caputo, P. Corbo, Xanthan and κ -carrageenan based alkaline hydrogels as electrolytes for Al/air batteries, *Carbohydrate polymers*, 157 (2017) 122-127.
- [7] F. Sharifi, S. Ghobadian, F.R. Cavalcanti, N. Hashemi, Paper-based devices for energy applications, *Renewable and Sustainable Energy Reviews*, 52 (2015) 1453-1472.