Improved Energy Efficiency of Lithium-Air Batteries by using Alloy Based Anode and Photocatalyst Loading Cathode

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Abstract: The development of high energy density batteries has been rapidly advanced by the increasing energy demand of the modern world. The lithium-air batteries have great interest due to their having the highest energy density compared to the other battery technologies. However, the large implementation of lithium-air batteries is hindered using metallic Li anode, leading to low coulombic efficiency, low energy efficiency and safety problems. In this study, to improve the performances of these batteries, we designed the lithium-air battery by integrating the Li-Si based alloy anode and photo-catalyst loading porous carbon cathode. The results show that the designed lithium-air battery has low over potential through the extended cycling stability. The working voltage of the cell is below 2.5 V. This study indicates that the developed the lithium-air battery with higher coulombic efficiency and lower polarization values is the alternatives to the conventional lithium-air batteries, which comprise metallic Li anode and carbon-based cathode.

Keywords: Alloy anode, Photoassisted charging, Lithium-air battery

Introduction

Li-air batteries have attracted great research attention because of their theoretically promising energy density in addressing the expanding energy storage demand (Imanishi & Yamamoto, 2019). However, there are numerous technical obstacles to developing an efficient lithium-air battery. Mainly, the Li-air cells have a low practical specific energy due to their poor rate capabilities (Wang et al., 2019). The high overpotentials that occur during the charge-discharge process in Li-air batteries cause low energy efficiency (Wang et al., 2019; Imanishi & Yamamoto, 2019). Due to the considerable electrode and electrolyte decomposition brought on by these high overpotentials, the Li-air cell life is quite short. On the other hand, using very reactive metallic lithium as an anode involves various problems such as dendritic growth, O₂ crossover and low coulombic efficiency (CE) in Li-air cells. In the literature, many studies have been carried out on anode, cathode and electrolyte in order to solve these problems (Wang et al., 2019).

Among the developed strategies related to the anode side, the use of alloy anodes is considered as very promising in elimination of many handicaps arise from the use of metallic Li anode without sacrificing the theoretical specific capacity (Li et al., 2020). Another strategy developed in Li-air batteries is to both reduce the charging voltages (<4.2 V) and extend the cycle life by using bifunctional cathodes which is quite an interesting approach. These bifunctional cathodes are formed by integrating photocatalytic (semiconductor) materials into the carbon matrix. The use of these bifunctional cathodes also introduced the concept of photo-assisted charging of Li-air batteries. During the photo-assisted charging process, electrons and holes are produced as a result of
light's excitation of the semiconductor. Due to the greater potential of the semiconductor's valence band (VB),
the holes have the ability to convert the reduction state cathode into an oxidation state cathode. On the other
hand, with the help of external electrical bias, the photo-generated electrons can convert $M^+$ to metallic $M$ at the
anode (Yan & Gao; 2022).

Herein, we developed the metal-air cell by integrating the Li-Si based alloy anode and photo-catalyst loading
porous carbon cathode (g-C$_3$N$_4$/rGO) to improve the performances of Li-air batteries. The usage of a
bifunctional cathode with Li-Si based alloy anode in the Li-air battery resulted in a considerable reduction in the
charge potential and improved the battery cyclic performance.

**Method**

Li$_{22}$Si$_5$ alloy was synthesized by mechanical alloying. Silicon powders and Li granules were weighted in Ar
atmosphere in the stoichiometric ratios. The mixtures of the powders were then put into a stainless steel vial
together with the stainless steel balls in the ball to powder ratio of 100:1. The mechanical alloying was carried
out by using planetary ball mill (Fritsch Pulverisette 7 Premium Line) at 500 rpm for 2 h. To prepare g-C$_3$N$_4$/rGO
bifunctional cathode, melamine and rGO were mixed in methanol. After complete mixing and drying
step, melamine and rGO were put in a crucible with a cover and heated up to 550 °C at a rate of 3 °C min$^{-1}$
under Ar atmosphere and then kept at this temperature for 3 h. The more detailed active material syntheses are
reported in our previous works (Lökçü et al., 2021; 2022).

The alloy anode was prepared by mixing the as-synthesized alloy with Cu powders (40:60 vol%) by using the
planetary ball mill and then they were pressed into a pellet with a diameter of 15 mm in the glove box. The
cathodes were prepared by mixing g-C$_3$N$_4$/rGO and poly (vinylidene fluoride) (PVDF) (80:20 wt%) in the 1-
methyl-2-pyrrolidone (NMP).

The discharge and charge tests were performed in 0.5 M LiClO$_4$:TEGDME:0.05 M LiI electrolyte
galvanostatically, and the discharge cutoff potential was 2.0 V Li$^+$/Li. The charge cutoff potentials were 3.6 and
4.2 V Li$^+$/Li for the photoassisted and dark charging, respectively.

**Results and Discussion**

The developed metal-air cells were discharged and charged at 200 mA g$^{-1}$ for 50 cycles to investigate their
cyclic stability and energy efficiency. Figure 1 shows the electrochemical performance of the cell under dark
charging conditions. Compared to metallic lithium in Li-air batteries, the discharge potential of the battery has
decreased from 2.8 V Li/Li$^+$ - 2.7 V Li/Li$^+$ (1) band to 2.6 V Li/Li$^+$ - 2.5 V Li/Li$^+$ band when the Li$_{22}$Si$_5$ alloy
anode is used (In Figure1). However, the decrease in capacity value in this cell started at the end of 16 cycles.
Moreover, the overpotential value of the cell, which was initially 0.7 V, increased to 1.7 V with the increasing
number of cycles.

![Figure 1. Discharge and charge curves gathered at 2500 mA h g$^{-1}$ (0.25 mA h cm$^{-2}$) fixed capacity and 200 mA
g$^{-1}$ (2x10$^{-2}$ mA cm$^{-2}$) current density under dark charging conditions for 50 cycles.](image-url)
Figure 2 shows the electrochemical performance of the cell under photoassisted charging conditions. While the charge potential decreases with the aid of visible light in the photoassisted charging process, it can also increase the discharge potential by the same mechanism. Obviously, photoassisted charging opens a new pathway to overcome the high overpotential problem in the Li-air batteries (Lökçü et al., 2022; Yu et al., 2014). Furthermore, the cell maintains its 2500 mA h g⁻¹ capacity for 50 cycles. Hence, the electrochemical performance of the developed metal-air cell with Li₂₂Si₅ alloy anode and bifunctional cathode improves considerably under photoassisted charging conditions.

![Photoassisted charging](image)

Figure 2. Discharge and charge curves gathered at 2500 mA h g⁻¹ (0.25 mA h cm⁻²) fixed capacity and 200 mA g⁻¹ (2x10⁻² mA cm⁻²) current density under photoassisted charging conditions for 50 cycles.

**Conclusion**

The developed metal-air cell with lower polarization values is the alternative to the lithium-air batteries configuration, which comprise a metallic Li anode and carbon-based cathode. This work demonstrated that the photoassisted charging with the efficient bifunctional cathode may open an essential path for the researchers to conduct extensive studies to approach the ultimate goal of commercializing Li-air batteries.

**Scientific Ethics Declaration**

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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**References**


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