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

Ersu LOKCU
Eskisehir Osmangazi University

Resat Can OZDEN
Eskisehir Osmangazi University

Mustafa ANIK
Eskisehir Osmangazi University

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, O_2 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 to 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

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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_3N_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_3N_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_3N_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^+ () 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.

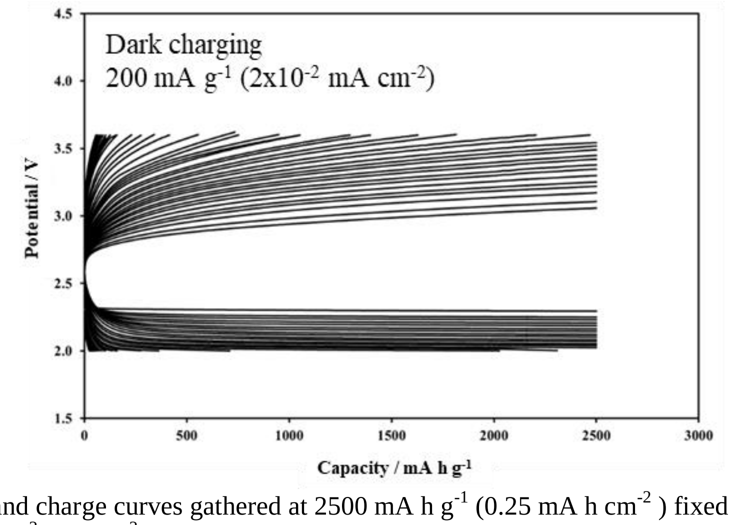

Figure 1. Discharge and charge curves gathered at 2500 mA h g^{-1} (0.25 mA h cm^{-2}) fixed capacity and 200 mA g^{-1} ($2x10^{-2}$ mA cm^{-2}) current density under dark charging conditions for 50 cycles.

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 $Li_{22}Si_5$ alloy anode and bifunctional cathode improves considerably under photoassisted charging conditions.

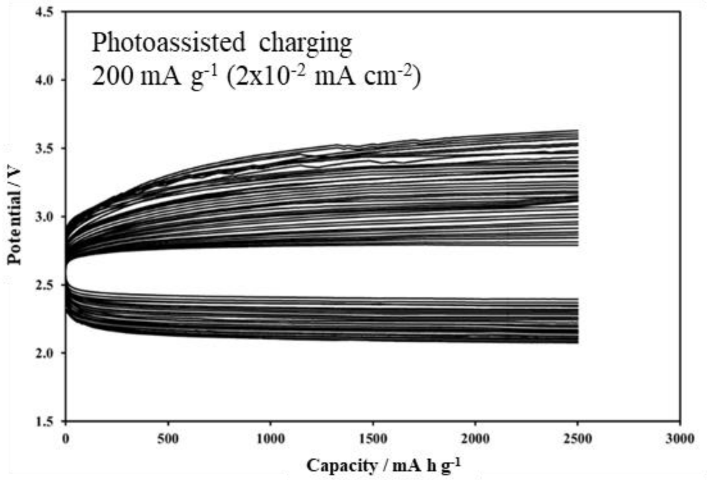

Figure 2. Discharge and charge curves gathered at 2500 mA h g^{-1} (0.25 mA h cm^{-2}) fixed capacity and 200 mA g^{-1} ($2x10^{-2}$ mA cm^{-2}) current density under photoassisted charging conditions for 50 cycles.

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

Imanishi, N., & Yamamoto, O. (2019). Perspectives and challenges of rechargeable lithium–air batteries. *Materials Today Advances*, *4*, 100031. https://doi.org/10.1016/j.mtadv.2019.100031

Lökçü, E., & Anik, M. (2021). Synthesis and electrochemical performance of lithium silicide based alloy anodes for Li–ion oxygen batteries. *International Journal of Hydrogen Energy*, *46*(18), 10624–10631. https://doi.org/10.1016/j.ijhydene.2020.12.179

Lökçü, E., Kaçar, N., Çayirli, M., Özden, R. C., & Anik, M. (2022). Photoassisted charging of li-ıon oxygen batteries using g-c3n4/rgo nanocomposite photocatalysts. *ACS Applied Materials and Interfaces*, *14*(30), 34583–34592. https://doi.org/10.1021/acsami.2c05607

Li, H., Yamaguchi, T., Matsumoto, S., Hoshikawa, H., Kumagai, T., Okamoto, N. L., & Ichitsubo, T. (2020). Circumventing huge volume strain in alloy anodes of lithium batteries. *Nature Communications*, *11*(1), 1–8. https://doi.org/10.1038/s41467-020-15452-0

Wang, C., Xie, Z., & Zhou, Z. (2019). Lithium-air batteries: Challenges coexist with opportunities. *APL Materials*, *7*(4). https://doi.org/10.1063/1.5091444

Yan, N., & Gao, X. (2022). Photo-assisted rechargeable metal batteries for energy conversion and storage. *Energy and Environmental Materials*, *5*(2), 439–451. https://doi.org/10.1002/eem2.12182

Yu, M., Ren, X., Ma, L., & Wu, Y. (2014). Integrating a redox-coupled dye-sensitized photoelectrode into a lithium-oxygen battery for photoassisted charging. *Nature Communications*, *5*(May), 1–6. https://doi.org/10.1038/ncomms6111

Author Information

Ersu Lökçü
Eskisehir Osmangazi University
Department of Metallurgical and Materials Engineering, 26040,
Eskisehir, Turkey
Contact e-mail: *elokcu@ogu.edu.tr*

Resat Can Ozden
Eskisehir Osmangazi University
Department of Metallurgical and Materials Engineering, 26040,
Eskisehir, Turkey

Mustafa Anik
Eskisehir Osmangazi University
Department of Metallurgical and Materials Engineering, 26040,
Eskisehir, Turkey

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