ScienceDirect

Applied Surface Science
Volume 586, 1 June 2022, 152806

Full Length Article

Organosilane based artificial solid electrolyte interface layer for stable metallic lithium anode

H. Irfan, A.M. Shanmugharaj

Show more

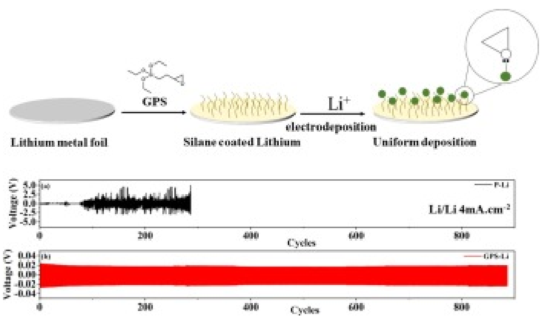
Share Cite

https://doi.org/10.1016/j.apsusc.2022.152806
Get rights and content

Abstract

Owing to its high specific capacity, lithium metals are considered as potential anode candidate for high energy density lithium-sulfur (Li-S)/lithium-oxygen (Li-O_2) batteries. However, uncontrollable lithium dendrite growth makes the spontaneously formed solid electrolyte interface layer (SEI) in lithium metal anode (LMA) fragile, preventing cyclic Li plating/stripping process, thereby limiting its usage in high energy density batteries. In this work, we demonstrate a novel organosilane coating strategy, resulting in the formation of artificial SEI (A-SEI) promoting stable operation of LMA. The presence of epoxide moieties in the coated organosilane induces uniform Li^+ electrodeposition, thereby effective control over dendrite growth. Symmetric Li/Li cells fabricated using silane coated lithium metal renders stable cycling with the constant over potential value of 40 mV over 800 cycles at the current rate of 4 mA cm^{-2}, when compared to pristine lithium anode. Furthermore, the NMC/Li cell fabricated using modified LMA showed relatively better charge/discharge capacity values of 116/115 mAhg^{-1} coupled with the coulombic efficiency of 99.1 %, after 200 cycles at 2C in comparison to pristine lithium based cell (charge/discharge capacity, 91/90 mAhg^{-1} @2C after 200 cycles). Thus, the proposed A-SEI coating strategy enrooted a new pathway for the development of lithium anodes with outstanding electrochemical characteristics.

Graphical abstract



Download : Download high-res image (109KB)
Download : Download full-size image

Introduction

For the past few decades there is constantly an increasing demand for developing energy conversion and storage materials, Eg., solar cells, hydrogen storage materials, low and high temperature fuel cells, and high energy density batteries. Among them, much attention has been drawn to lithium-ion (Li^+ ion) batteries (LIBs) due to the range of applications in the portable electronic gadgets [1], [2], [3]. However, the development of high-energy density batteries for electric vehicle applications using existing battery technology is severely hampered due to the low theoretical capacity of the graphite anode (~372 $mAhg^{-1}$). Extensive research has been done on nanostructured inorganic anodes to replace the graphite anodes in current state-of-art lithium battery technology [4], [5], [6]. In addition, recent attempts on metal foil anodes such as tin (~994 $mAhg^{-1}$), zinc (~410 $mAhg^{-1}$), aluminum (~993 $mAhg^{-1}$), and magnesium (~3350 $mAhg^{-1}$) provide a positive glimpse in the fabrication of high energy density batteries, however, several parameters need to be optimized for the same.

The unique features of lithium metal anodes viz., high specific capacity (~3861 $mAhg^{-1}$), low density (~0.53 $g.cm^{-3}$), and extremely low anode potential (−3.04V vs. standard hydrogen electrode) make it a potential candidate for the development of high energy density batteries [7], [8]. However, dendrite growth is a very common phenomenon observed in the lithium metal anodes, due to the preferential electrodeposition on the selective spots of the metal surface resulting in the needle-like configuration during the electrochemical charge/discharge cycling. Low coulombic efficiency, faster consumption of electrolyte, and rapid capacity fading are the serious outcomes of the uncontrolled electrodeposition, thereby dendrite growth during Li^+ ion plating/stripping process, promoting battery short circuit and even catastrophic failure [9].

An efficient approach in solving the fundamental problem remains elusive and many research attempts have been made to control the formation of dendrites in lithium metal batteries [10], [11], including solid-state electrolyte (SSE) [12], [13], artificial solid electrolyte interface layer (A-SEI) [14], electrostatic shield mechanism [15], anion tethering [16], electrolyte additive [9], [17], functional separator [18], [19] etc. Among all these techniques, the fabrication of an artificial solid electrolyte interface layer (A-SEI), which can also be called as ex-situ SEI is the most efficient pathway in suppressing the dendrite growth, thanks to its electronically insulating but ionically (Li^+ ion) conducting nature. Recently, Amine et.al, [20] demonstrated the stable cycling performance for over 3000 cycles at current density 1 $mA.cm^{-2}$ by depositing Lithium phosphorous oxynitride (LIPON) A-SEI layer directly on the Li metal surface using atomic layer deposition (ALD) technique. A. Hu et al.[21] reported the effectiveness of the hybrid LiF/Li_3Sb A-SEI layer for stabilizing the Li metal anode at a high current for practical application. In contrast to robust, thin and protective in-situ SEI, which formed due to the reductive decomposition of the solvents, ex-situ SEI layer forms a thick coating at the lithium surface, which however, hampers its self-healing ability and it needs to be addressed.

Though extensive work has been done on A-SEI layer stabilized lithium anode, no reports depicting the role of organosilane coating on the mechanism of lithium dendrite control has been proposed. Organosilane modification on lithium metal prevents solvent induced surface changes, thereby ensuring extended cycle life when used as an anode in LIBs. Even though, the first report on Li metal stabilization using silane-based coatings provided a positive glimpse in making long cycle life lithium metal batteries, however, the detailed experimental investigation needed to correlate the interfacial chemistry to the performance characteristics of the lithium metal batteries [22]. The present paper discusses the role of organosilane consisting of epoxide moieties (3-Glycidoxypropyltrimethoxysilane) as an A-SEI layer on lithium anode in controlling the Li dendrite growth during electrochemical cycling. Detailed structural, chemical, morphological and electrochemical characterization of silane modified lithium has been done to corroborate its self-regulating, ensuring long cycling stability, when used as an anode in LIBs.

Section snippets

Experimental

Lithium metal is obtained and stored in an argon atmosphere glovebox. Lithium metal (Obtained from Sigma Aldrich Inc., USA) was scratched abrasively to remove the oxidized layer. Then the scratched lithium foil was subjected to coating process by immersing it in 5 ml of (3-glycidoxypropyltrimethoxysilane (Procured from Sigma Aldrich Inc., USA) for 10 min followed by drying at 100°C for 1 h. From now on the prepared samples are designated as P-Li (Pristine Lithium foil) and GPS-Li (Silane…

Results and discussions

Displayed in Fig. 1 (a) is the schematic representation of the preparation steps of 3-glycidylpropyltriethoxysilane coated lithium foil (GPS-Li) as well as the possible dendrite suppression phenomena in comparison to P-Li (Fig. 1 (b & c)). Owing to its low density (~0.53 g/cm^3) as well as its high reactivity nature, pristine lithium (P-Li) consists of several grey colored patches due to the formation of lithium hydroxide (Li-OH) and lithium carbonate (Li_2CO_3) groups on its surface. Organosilane …

Conclusions

In summary, a novel organosilane based A-SEI coating strategy for controlling dendrite growth in the lithium anode has been proposed. In comparison to pristine lithium anode, coated anode enables a stable Li plating/stripping process with the control over the lithium dendrite growth, resulting outstanding electrochemical performance. Li/Li symmetric cells fabricated using organosilane coated lithium showed uniform Li plating/stripping process without noticeable voltage fluctuations at the…

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

Acknowledgements

The authors are thankful to the Department of Science and Technology-Materials for Energy Storage, New Delhi, India. (DST/TMD/MES/2K18/139) for the financial support of this study. The authors also would like to thank Dr. M. Devendiran, Central Instrumental Laboratory, VISTAS, Pallavaram, Chennai for performing instrumental characterizations. The fellowship from DST-MES is also thankfully acknowledged by H Irfan.…

Recommended articles

References (40)

N. Nitta *et al.*
Li-ion battery materials: present and future
Mater. Today (2015)

X. Xu *et al.*
Recent progresses in the suppression method based on the growth mechanism of lithium dendrite
J. Energy Chem. (2018)

N. Munichandraiah *et al.*
Surface films of lithium: An overview of electrochemical studies
J. Power Sources (1998)

F. Zheng *et al.*
Review on solid electrolytes for all-solid-state lithium-ion batteries
J. Power Sources (2018)

W. Ren *et al.*

Recent progress of functional separators in dendrite inhibition for lithium metal batteries
Energy Storage Mater. (2021)

K. Amine *et al.*
Novel silane compounds as electrolyte solvents for Li-ion batteries
Electrochem. Commun. (2006)

R.S. Thompson *et al.*
Stabilization of lithium metal anodes using silane-based coatings
Electrochem. Commun. (2011)

N. Fairley *et al.*
Systematic and collaborative approach to problem solving using X-ray photoelectron spectroscopy
Appl. Surf. Sci. Adv. (2021)

G. Greczynski *et al.*
X-ray photoelectron spectroscopy: towards reliable binding energy referencing
Prog. Mater. Sci. (2020)

J.C. Wang *et al.*
Model for the interfacial impedance between a solid electrolyte and a blocking metal electrode
Solid State Lonics (1986)

View more references

Cited by (11)

Lithium deposition stability using TiO<inf>2</inf>/MWCNT as artificial solid-electrolyte interphases in gel polymer electrolytes based lithium metal batteries
2023, Electrochimica Acta

Show abstract

The effect of the SEI layer on the electrochemical impedance in the graphite/Li[Ni<inf>0.5</inf>Mn<inf>0.3</inf>Co<inf>0.2</inf>]O<inf>2</inf> lithium-ion full cells
2023, Applied Surface Science

Show abstract

Growing cuprite nanoparticles on copper current collector toward uniform Li deposition for anode-free lithium batteries
2023, Applied Surface Science

Show abstract

Constructing methyl methacrylate/MXene artificial solid-electrolyte interphase layer for lithium metal batteries with high electrochemical performance
2022, Applied Surface Science

> *Citation Excerpt :*
> …However, one great challenge of LMBs is the uneven deposition of lithium ions on the surface of lithium metal, after continuous plating and stripping, resulting in the formation of lithium dendrites. These dendrites can easily puncture the membrane and destabilize the interface between electrode and electrolyte, leading to low Coulombic efficiency, short circuit or even explosion [4–9].

In order to solve these problems, many strategies have been employed such as the anode structure strategy [9–14], modification of the interface between electrolyte and electrode [15–21], and usage of solid-state electrolytes(SSEs) [22–26], etc.…

Show abstract

Semi-solid lithium/oxygen flow battery: an emerging, high-energy technology

2022, Current Opinion in Chemical Engineering

Citation Excerpt :

…The membrane is also an important component of LAB and it should be designed properly to avoid or limit the O2 crossover from the cathode to the anode [4–8]. One of the major challenges for the cycle life of LAB cells is the durability of the Li metal electrode, and several strategies were proposed to increase cell cyclability and safety [9–12]. At the cathode side, during the discharge and recharge processes, the peroxide species are formed and re-oxidized to O2.…

Show abstract

Perspectives of High-Performance Li–S Battery Electrolytes ↗

2024, Advanced Functional Materials

View all citing articles on Scopus ↗

View full text