



Research papers

Preparation of g-C₃N₄/ZIF-8/PVDF-modified Li anode for all-solid-state Li metal batteriesKumlachew Zelalem Walle^{a,b,c}, Yi-Shiuan Wu^a, She-Huang Wu^d, Wen-Chen Chien^b, Jeng-Kuei Chang^g, Rajan Jose^e, Chun-Chen Yang^{a,b,f,*}^a Battery Research Center of Green Energy, Ming Chi University of Technology, New Taipei City 24301, Taiwan, ROC^b Department of Chemical Engineering, Ming Chi University of Technology, New Taipei City 24301, Taiwan, ROC^c University of Gondar, Department of Chemistry, Gondar, Ethiopia^d Graduate Institute of Science and Technology, National Taiwan University of Science and Technology, 43, Sec. 4, Keelung Road, Taipei 106, Taiwan, ROC^e Nanostructured Renewable Energy Materials Laboratory, Faculty of Industrial Sciences and Technology, University Malaysia Pahang, 26300 Kuantan, Malaysia^f Department of Chemical and Materials Engineering, and Green Technology Research Center, Chang Gung University, Taoyuan City 333, Taiwan, ROC^g Department of Materials Science and Engineering, National Yang Ming Chiao Tung University, 1001 University road, Hsinchu, 30010, Taiwan, ROC

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ABSTRACT

All-Solid-state lithium metal batteries (ASSLMBs) are promising next-generation energy storage devices. However, the formation of lithium (Li) dendrites in ASSLMBs limits their applications. In this study, we used an inorganic/organic mixture of graphitic carbon nitride (g-C₃N₄), zinc-based Zeolitic Imidazolate Framework-8 (ZIF-8), and poly(vinylidene difluoride) (PVDF)—g-C₃N₄/ZIF-8/PVDF (g-CNZP)—to modify the surface of a lithium metal anode (LMA). The 2032-type coin cell was assembled based on a lithium Nafion (LiNF)-coated NCM811 (denoted as LiNF@NCM811) cathode, inorganic/organic mixture modified Li metal anode (LMA) (denoted g-CNZP@Li), and a LiNF-coated Li_{6.05}Ga_{0.25}La₃Zr₂O_{11.8}F_{0.2} (LiNF@LG_{0.25}LZOF) filler in bilayer hybrid solid electrolyte (Bi-HSE). The coin cell was charged between 2.8 and 4.2 V at 0.5C exhibited an initial specific discharge capacity of 134.45 mAh g⁻¹ and retained 86.1 % of its capacity after 280 cycles at 30 °C. The average coulombic efficiency of the cell was approximately 99.8 %. Furthermore, the high-voltage (2.8–4.5 V, at a rate of 0.2C) result also delivered an initial specific discharge capacity of 194.3 mAh g⁻¹ and, after 100 cycles, maintained 81.8 % of its initial capacity at room temperature. The presence of the nanosheet/nanoparticle composite coating material on the LMA surface suppressed Li dendrite growth and enhanced the compatibility between the LMA and Bi-HSE membrane. In addition, the *in-situ* formation of Li₃N on the solid electrolyte interface (SEI) layer improved the ionic conductivity and ensured intimate interfacial contact during cycling. Therefore, these novel bi-layered fabrication strategies for obtaining hybrid/composite solid electrolyte membranes and modifying LMA surfaces via 2D g-C₃N₄ material with ZIF-8 MOFs and PVDF composites appear to have applicability in the preparation of very safe high-voltage cathodes for ASSLMBs.

1. Introduction

With their long cycle lives and high energy densities, lithium-ion batteries (LIBs) have received much attention as alternatives to conventional energy storage systems. Because conventional liquid electrolyte battery systems can be highly flammable and susceptible to liquid leakage, solid-state electrolytes (SSEs) have promise for improving the safety of LIB systems [1]. SSEs appear in many forms, including solid polymer electrolytes (SPEs), inorganic solid electrolytes (ISEs), and hybrid/composite polymer electrolytes (HSEs) [2]. SPEs comprise a

polymer matrix mixed with lithium salts; consequently, they are easy to process, have good flexibility and offer safe performance and good interfacial contact with electrodes [3,4]. Nevertheless, SPEs exhibit low ionic conductivity, inferior thermal and electrochemical stabilities, and unsatisfactory behavior in their ability to suppress lithium dendrite growth. In comparison, ISEs display higher ionic conductivities, a wide electrochemical window, and high mechanical strength, but provide poor interfacial contact with electrodes [4,5]. These various disadvantages of SPEs and ISEs severely restrict their commercial applications in powering lithium batteries. HSEs constructed from SPEs and inorganic

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