



A polydopamine-modified garnet-based polymer-in-ceramic hybrid solid electrolyte membrane for high-safety lithium metal batteries

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ABSTRACT

Composite solid electrolyte (CSE) membranes combining the attractive properties of ceramic and polymer-based electrolytes have emerged as preferred electrolytes for all-solid-state lithium metal batteries (ASSLMBs). In this study, we used solution-casting to prepare a CSE membrane from a suspension of polydopamine (PDA)-modified $\text{Li}_{6.28}\text{La}_3\text{Zr}_2\text{Al}_{0.24}\text{O}_{12}$ (LLZAO) filler (PDA@LLZAO), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and succinonitrile (SN) as the middle layer and a matrix of PVDF-HFP, LiTFSI, and SN as both the top and bottom layers. The presence of PDA on the surface of LLZAO enabled the filler to percolate well within the polymer matrix. Consequently, a membrane based on PDA@LLZAO (CSE1) exhibited high ionic conductivity ($4.01 \times 10^{-4} \text{ S cm}^{-1}$), a high lithium transference number (ca. 0.76), high tensile strength (29.09 MPa), and a stable electrochemical window (ca. 5.01 V vs Li/Li⁺) relative to those properties of a counterpart membrane (CSE0) having the same constituents as CSE1, but an unmodified LLZAO filler. The interfacial stability developed by the synergetic effect of the CSE1 membrane and Li metal anode enhanced the corresponding Li plating/stripping performance (2000 h) and critical current density (2.0 mA cm^{-2}). Benefiting from this stable interfacial contact, an Al_2O_3 @NCM811/CSE1/Li coin-type cell provided a discharge specific capacity of 136.46 mAh/g at a rate of 0.5C after 300 cycles, with a capacity retention of 86.22 % and a average coulombic efficiency of 99.16 % at 25 °C. Hence, our proposed strategy for preparing CSEs appears to be promising for use in ASSLMB applications.

1. Introduction

Imbalances in electrical energy supply and demand for household appliances, electric vehicles, and portable electronics can lead to electrical power fluctuations and shortages, due to limited energy densities [1,2]. Hence, alternative energy storage devices—most notably lithium-ion batteries (LIBs)—have become valuable because of their relatively high volumetric and gravimetric energy densities [3]. Although conventional liquid-type electrolytes have been used for many years as media for Li⁺ ion transmission (because they provide rapid ion movement, high surface wettability with the electrodes, and satisfactory rate performance [4,5]), associated safety concerns (e.g., electrolyte leakage,

high toxicity, thermal runaway, non-reversible electrolyte decomposition, electrolyte instability with electrodes, and lithium dendrite formation [4,6,7]) have affected the wider practical applications of lithium-metal batteries (LMBs). Among the various energy storage candidates, all-solid-state electrolytes have attracted great attention for their good safety characteristics, long cycle lives, broad and stable electrochemical windows, lower degrees of lithium dendrite formation, and limited catastrophic failures [8]. There are two broad categories of solid-state electrolytes: those based on polymers and those based on ceramic materials [9].

Solid polymer electrolytes (SPEs) can be fabricated by solubilizing single or blended polymers with lithium-containing salts in appropriate

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