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Optimized ion-conductive pathway in UV-cured solid polymer electrolytes for all-solid lithium/sodium ion batteries

Jin Il Kim [a], Young Gyun Choi [a], Yeonho Ahn [b], Dukjoon Kim [b], Jong Hyeok Park [a,*]

[a] Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul, 120-749, Republic of Korea
[b] School of Chemical Engineering, Sungkyunkwan University, Suwon, Gyeonggi, 16419, Republic of Korea

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ABSTRACT

Solid electrolyte-based lithium-ion batteries (LIBs) have enormous potential to replace conventional LIBs with flammable liquid electrolytes. However, most solid electrolytes show low ionic conductivity and poor interfacial properties with electrodes, preventing them from reaching the level of conventional liquid electrolyte systems with separators. Herein, we optimized the formation of an ion-conductive pathway in a UV-cured solid polymer electrolyte (USPE) via a semi-interpenetrating polymer network with a minimal liquid content. The USPE consists of a UV-curable hard matrix (trimethylolpropane ethoxylate triacrylate, ETPTA) as a backbone film with negligible ionic conductivity and an optimized ionic channel with an ion-solvated gel polymer (Li^+/PVdF-HFP) with a minimal liquid content for boosting the Li^+ conduction. The hybrid solid-state film provides high ionic conductivity (up to 85%) relative to commercial liquid electrolyte systems and a stable electrochemical window. We also applied the same USPE with Na^+ for solid electrolyte-based sodium ion batteries, and similar positive effects were also observed. Going another step forward, both the PVdF-HFP/ETPTA ratio and the HFP content in the PVdF-HFP are critical gel polymer additives for generating reinforced Li^+ ion pathways in USPE.

1. Introduction

Lithium-ion batteries (LIBs) with their high energy density and large potential range have been studied for decades and are now the leading choice for industrial energy storage systems in electronic mobile devices and vehicles [1–6]. LIBs are composed of electrodes (a cathode and an anode), an electrolyte, and a separator, and most studies focus on the electrodes because the electrodes determine the theoretical charging/-discharging capacity of LIBs [7–11]. Non-aqueous electrolytes, composed of lithium salts and organic solvents, are commonly used in LIBs because of their fast ion conduction from the liquid phase. However, organic liquid electrolytes have serious drawbacks, such as leakage problems and flammability issues resulting from their volatility [12–14]. Thus, the development of substitutable electrolytes that are not explosive is essential for the reliable operation of LIBs.

Gel electrolytes, which contain polymeric materials for entrapping liquid electrolytes, are an alternative to conventional organic liquid electrolytes [15,16]. Poly (vinylidene fluoride-cohexafluoropropylene) (PVdF-HFP) copolymer, a representative gel electrolyte, has good entrapping properties and thermal/electrochemical stability for applications in LIBs [15,17,18]. Amorphous voids in the semicrystalline region of the HFP constituents in the PVdF-HFP contribute to its excellent entrapping ability, showing favorable interactions with organic liquid electrolytes, and this material could advance gel electrolytes and partially solve the leakage problem, improving the electrochemical characteristics of LIBs [19]. However, gel electrolytes involve a substantial amount of liquid and have poor mechanical durability, and thus safety concerns due to their volatility remain.

Solid polymer electrolytes with ion conductive properties have emerged recently as a strategy or avoiding these problems because solid polymer electrolytes have the advantages of reasonable flexibility and better interfacial compatibility with electrodes [20–22]. Polyethylene oxide (PEO) is a typical polymer for solid polymer electrolytes because its ethylene oxide (EO) unit has high chain flexibility and Li^+ donor number, causing improved Li^+ conduction [23–25]. However, there is a limit to how much PEO can be used in practical applications due to its low Li^+ ionic conductivity because of its high crystallinity. To address this challenge [25], many studies on PEO have been reported, and their Li ion conduction has been improved by reducing the crystalline regions [26,27] and regulating PEO derivatives [28]. Another approach to preparing solid polymer electrolytes is the curing method by adding an external energy source such as UV irradiation to a monomer that

* Corresponding author.
E-mail address: lutts@yonsei.ac.kr (J.H. Park).

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