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Anionic three-dimensional porous aromatic framework for fast Li-ion conduction

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ABSTRACT

Solid polymer electrolytes (SPEs) have been received significant attention due to their inherent advantages of high safety and high electrochemical stability as fast Li-ion conductors. However, conventional SPEs of dual-ion conductors (*i.e.*, conducting both anions and cations) are prone to induce concentration polarization and thus decrease in ionic conductivities, which remains a significant hurdle for their practical applications. Here, we propose a new host of porous aromatic frameworks (PAFs) as a promising single Li-ion conducting SPEs. PAF1 is one of the promising types for crystalline polymers with the integration of aromatic organic building units into a 3-dimensional framework, having plenty of voids space inside. By covalently tethering the sulfonate on aromatic groups, anions are immobilized onto the frameworks, and the exchanging process of protons with Li-ions makes it perform as a fast Li-ionic conductor. Consequently, Li sulfonated PAF1 (denoted as Li-SPAF1) shows superior ion-conducting properties of 0.102 mS cm^{-1} at room temperature with the activation energy of 0.21 eV. It is demonstrated that the aromatic groups have high chemical and thermal stabilities, even stable with Li metal, which is advantageous for delivering stable electrochemical performances. Also, the structure and conduction mechanism are theoretically investigated by using density functional theory calculations.

1. Introduction

During the last few decades, Li-ion batteries (LIBs) have been commonly used for electronic devices, especially in small and portable applications. Although there have been significant advances in LIBs, increasing market demand for a more efficient electrical energy source for large-scale applications, such as electric vehicles (EVs) and energy storage systems (ESSs), is actively driving the development of next-generation batteries with improved performance and enhanced safety [1–3]. For example, new energy storage systems with significantly higher energy density, such as Li-S, Li-air, and Li metal batteries, have been extensively studied [4–6]. However, their practical applications are still plagued by a critical safety issue, mainly originated from the use of flammable liquid electrolytes causing catastrophic fires or explosions

in the large-scale employment of the LIBs [7,8].

All-solid-state batteries using inorganic solid electrolyte (SE) are expected to solve the prevailing safety issue, and the non-flammability of SE could enhance the thermal and chemical stabilities of the solid-state-battery [9–11]. However, the inorganic SEs have their own limitations, including hardness and heaviness. In particular, the poor contact among hard solid particles inevitably results in the high interfacial resistance, which has been a critical hurdle for their practical applications [12]. Alternatively, solid polymer electrolytes (SPEs), which are composed of light-weighted polymer (or gel) host and conducting agents (*e.g.*, lithium salts) [13–15], start to stand out, since the flexible nature of SPEs helps to effectively reduce the interfacial resistance by forming an intimate contact with electrodes [16–19]. However, the dual-ion conducting nature of conventional SPEs (*i.e.*, conducting both anions

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