Ternary natural deep eutectic solvent (NADES) infused phthaloyl starch as cost efficient quasi-solid gel polymer electrolyte

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ABSTRACT

A first-of-its-kind, eco-friendly quasi-solid bioelectrolyte derived from potato starch was prepared. Starch was chemically modified via phthaloylation to synthesize amorphous, hydrophobic starch derivative and the attachment of the phthaloyl group was confirmed via FTIR which showed phthalate ester peak at 1715 cm⁻¹; and ¹H NMR peaks between 7.30–7.90 ppm attributed to the aromatic protons of the phthaloyl group. The resulting derivative was then infused with ternary natural deep eutectic solvent (NADES) made from different molar ratios of choline chloride, urea and glycerol. Electrochemical Impedance Spectroscopy (EIS) revealed that the highest ionic conductivity was obtained by the system consisting of NADES with choline chloride:urea:glycerol in molar ratios of 4:6:2, with a magnitude of 2.86 mS cm⁻¹, hence validating the prospects of the materials to be further experimented as an alternative electrolyte in various electrochemical devices.

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1. Introduction

Fabrication of starch based polymer electrolytes is currently an active area of research in electrochemistry. This category of electrolyte is especially appreciated for its cost efficiency, biodegradability and natural abundance, hence qualifying them as excellent substitutes to the conventional petroleum based polymer electrolytes (Manuel Stephan, 2006). However, the high crystallinity of starch in its natural state inhibits flexibility of the polymer chain and thus prevents the electrolyte from achieving high ionic conductivity. The high hydrophilicity of pristine starch also prevents it from being dissolved in most organic solvents and this limits the preparation of starch electrolyte to only solid films. Previously, phthaloylation of polysaccharides such as chitosan have been shown to be successful in imparting organosolubility and suppressing crystallinity (Yusuf et al., 2016). High ionic conductivity was achieved when this modified chitosan was used as the host in the fabrication of gel polymer electrolyte (Azzahari, Yusuf, Selvanathan, & Yahya, 2016). Thus, in this study, the hydrophilic and crystalline properties of pristine starch are reformed via a simple phthaloylation reaction and used as a component to fabricate a novel quasi-solid bioelectrolyte based on the starch derivative.

In recent times, quasi-solid polymer electrolytes are emerging as a unique class of electrolytes; highly celebrated for its good physical stability and high ionic conductivity. Conventionally, the fabrication of quasi-solid gel polymer electrolyte is achieved by incorporating organic solvents and lithium or sodium based ionic salts into the polymer host (Di Noto, Lavina, Giffin, Negro, & Scrosati, 2011; Hallinan & Balsara, 2013; Manuel Stephan, 2006). Recently, the inclusion of imidazolium based ionic liquids was also performed in preparing gel electrolytes with high ionic conductivities (Karuppasamy et al., 2016; Ortega, Trigueiro, Silva, & Lavall, 2016). However, such approach elevates the preparation cost while at the same time threatens the biodegradability of the electrolyte.

Deep eutectic solvents (DES) are gaining vast attention since they exhibit similar physico-chemical properties to traditional imidazolium based ionic liquids and therefore advantageously replace them in many applications. The low ecological footprint, ease of preparation and economical price of deep eutectic solvents as compared to ionic liquids could promote their usage on a large-scale (Zhang, De Oliveira Vigier, Royer, & Jerome, 2012; Dai, van Sprosen, Witkamp, Verpoorte, & Choi, 2013). In this