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An ether-functionalised cyclic sulfonium based ionic liquid as an electrolyte for electrochemical double layer capacitors

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HIGHLIGHTS

- A novel ether-functionalised cyclic sulfonium IL, [THT_{G1}][TFSI], was synthesised.
- Transport properties promoted by ether moiety relative to an alkyl-based analogue.
- Electrochemical/thermal stability [THT_{G1}][TFSI] not inhibited by ether moiety.
- [THT_{G1}][TFSI] used as solvent-free electrolyte in EDLC at 2.6 V.

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ABSTRACT

A novel cyclic sulfonium cation-based ionic liquid (IL) with an ether-group appendage and the bis{(trifluoromethyl)sulfonyl}imide anion was synthesised and developed for electrochemical double layer capacitor (EDLC) testing. The synthesis and chemical-physical characterisation of the ether-group containing IL is reported in parallel with a similarly sized alkyl-functionalised sulfonium IL. Results of the chemical-physical measurements demonstrate how important transport properties, *i.e.* viscosity and conductivity, can be promoted through the introduction of the ether-functionality without impeding thermal, chemical or electrochemical stability of the IL. Although the apparent transport properties are improved relative to the alkyl-functionalised analogue, the ether-functionalised sulfonium cation-based IL exhibits moderately high viscosity, and poorer conductivity, when compared to traditional EDLC electrolytes based on organic solvents (propylene carbonate and acetonitrile). Electrochemical testing of the ether-functionalised sulfonium IL was conducted using activated carbon composite electrodes to inspect the performance of the IL as a solvent-free electrolyte for EDLC application. Good cycling stability was achieved over the studied range and the performance was comparable to other solvent-free, IL-based EDLC systems. Nevertheless, limitations of the attainable performance are primarily the result of sluggish transport properties and a restricted operative voltage of the IL, thus highlighting key aspects of this field which require further attention.

1. Introduction

Electrochemical double layer capacitors (EDLCs), or supercapacitors, stand among the most promising energy storage technologies today [1]. EDLCs store energy by charge separation at the electrode/electrolyte interface rather than by reversible redox reactions as in metal ion batteries [2]. To date, the major challenge for EDLCs when compared to other energy devices is their limited energy density (<10 Wh kg^{-1}) [3], which currently is unable to meet the requirements of high energy density applications. To overcome this challenge, extensive work has been undertaken to increase the energy density of EDLCs which has been the subject of a number of recent reviews [3–7]. As the energy density is proportional to the capacitance and the square of the voltage, increasing the capacitance and/or the cell voltage is an effective way to increase the energy density. This can be achieved through the development of novel carbon materials for electrodes with high capacitance, such as templated carbide-derived carbons [8,9],

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carbon nanotube-based structures [10,11] and graphene-derived carbons [12]. Furthermore, alternative materials may be selected for the electrode structure to introduce pseudocapacitive charging contributions. These materials may combine transition metal oxides with conductive polymer coatings, such as Co_3O_4 in polypyrrole [13] and $MnFe_2O_4$ in polyaniline [14], which, by incorporating redox active pseudocapacitive processes, may increase the total achievable capacitance. Alternatively, the development of novel electrolytes with increased operating potential windows is an important strategy for improving the energy storage capabilities of devices relying on purely capacitive charge storage. Currently, the majority of commercial EDLCs use organic electrolytes based on acetonitrile or propylene carbonate (with a tetraethylammonium tetrafluoroborate, $[Et_4N][BF_4]$, salt) with a cell operating voltage of 2.5–2.8 V [3,15]. While the utilisations of these electrolyte formulations have been studied in-depth and optimised for application in EDLCs, the ultimate performance may be hindered by the limited solubility of traditional salts in the solvents. A higher solubility salt can be used to form more concentrated electrolytes to promote better electrolyte conductivities and limit the possible electrolyte depletion at the interface [3]. Additionally, higher salt concentrations within the electrolyte can be utilised to reduce the potentially hazardous volatility and flammability of such solvents and, in turn, improve the safety of an operating EDLC [16].

In this regard, ionic liquids (ILs) are presently considered as attractive electrolyte materials for the development of safer EDLCs due to their intrinsic chemical-physical properties including their non-volatility and good (electro)chemical stability. Recent studies indicate that applying ILs as EDLC electrolytes, such as 1-ethyl-3-methylimidazolium tetrafluoroborate, $[EMIm][BF_4]$, and 1-butyl-1-methylpyrrolidinium bis{(trifluoromethyl)sulfonyl}imide, $[Pyrr_{14}][TFSI]$, operative voltages of up to 3.7 V can be achieved [17–19]. However, as ILs exhibit higher viscosities and lower conductivities than electrolytes based on organic solvents, IL-based EDLCs typically display lower power outputs than conventional EDLCs, especially under ambient operating conditions [20]. In recent years several strategies have been proposed to improve the power of IL-based EDLCs, focusing on the use of mixtures of ILs and organic solvents to be one of the most effective approaches. These mixtures have included conventional solvents, propylene carbonate and acetonitrile [19,21–23], and several reports of novel solvents including a variety of mononitriles [24], adiponitrile (an aliphatic dinitrile solvent) [25,26], gamma butyrolactone [27] and amides [28]. In general, the introduction of the solvent is used to promote the transport capabilities of the electrolyte relative to the neat IL while still maintaining high concentrations of the ionic species and, in turn, improve capacitance of the IL-based EDLCs at high currents under ambient conditions.

Other approaches towards the improvement of ILs as electrolytes for EDLCs and other electrochemical energy storage devices can involve judicious tailoring of the cation-anion functionality to manipulate the chemical-physical properties of the IL. For example, incorporation of ether appendages (*e.g.* substitution of a butyl side chain for a similarly sized 2-methoxyethyl group) can in some instances contribute to the decrease of viscosity and melting point without drastically impacting on the electrochemical and thermal stability [29–31]. Similarly, careful selection of the structure of the anionic component, for example bulky fluorine-based anions with highly delocalised electron distributions, may be utilised to tailor the chemical-physical properties of the resulting IL [29,31]. For example, in view of an IL consisting of a 1-butyl-1-methylpyrrolidinium cation with a $[TFSI]^-$ anion (bulky, high charge delocalisation, flexible), the melting point and viscosity (254 K and 76 mPa s at 298 K, respectively) is significantly lower than for the analogous IL with a symmetrical, non-flexible $[BF_4]^-$ anion where the negative charge is more localised and the melting point is 423 K [29]. Alternatively, the application of ILs based on the fluorine-free dicyanamide anions, $[N(CN)_2]^-$, in EDLCs has also recently been reported [32]. In combination with pyrrolidinium based cations, the $[N(CN)_2]^-$-based ILs were reported to exhibit lower viscosity and higher conductivity than the $[TFSI]^-$-based analogues and, in turn, displayed very good power capabilities, and good capacity retention over 25,000 cycles when used as solvent-free EDLC electrolytes. Nevertheless, the electrochemical stability, and the operative voltage, of the $[N(CN)_2]^-$-based ILs was reported as lower than the $[TFSI]^-$ analogues, potentially limiting the available energy density of EDLC based on such an IL electrolyte.

Cations suitable for the implementation of innovative ILs include those based on sulfur which typically display lower viscosities in comparison to their analogous ammonium counterparts [33,34]. For example, at 298 K the reported viscosity and conductivity of $[TFSI]^-$-based ILs with an *S*-butyl-*S*-dimethylsulfonium cation (39.0 mPa s and 10.0 mS cm^{-1} at 298 K, respectively) is significantly improved relative to *N*-butyl-*N*-triethylammonium $[TFSI]^-$ (104.1 mPa s and 6.9 mS cm^{-1}, respectively); an analogous tetraalkylammonium cation-based IL of approximately similar size [34]. However, despite having a lower viscosity, higher conductivity and lower melting points, ILs based on trialkylsulfonium cations have attracted limited attention compared to their ammonium analogues. Nevertheless, several groups have reported work emphasising the use of cyclic [35–38] and acyclic [39–41] sulfonium ionic liquids as electrolytes for energy devices. Research surrounding the influence of ether functionalisation of the cation on the properties of sulfonium-based ILs has only been studied by Han et al. [42] wherein ILs based on the bis(fluorosulfonyl)imide anion, $[FSI]^-$, and small acyclic sulfonium cations with and without ether functionality were reported to exhibit low viscosities (20–30 mPa s at 298 K), good conductivities (8.2–15.7 mS cm^{-1} at 298 K) and reasonable electrochemical stability windows (*ca.* 4.2–4.8 V). Recently, we also reported the use of acyclic aprotic sulfonium ILs as potential electrolytes for EDLC devices [27].

With the aim to further develop and understand the limits related to the use of sulfonium-based ILs in supercapacitors, we investigated the chemical-physical properties of the alkyl and ether functionalised cyclic sulfonium ILs, *S*-butyltetrahydrothiophenium bis{(trifluoromethyl)sulfonyl}imide, $[THT_4][TFSI]$, and *S*-(2-methoxyethyl)tetrahydrothiophenium bis{(trifluoromethyl)sulfonyl}imide, $[THT_{G1}][TFSI]$. The electrochemical performance of EDLCs containing the novel ether-functionalised IL, $[THT_{G1}][TFSI]$, as a neat electrolyte was also investigated as a proof of concept.

2. Experimental

2.1. Synthesis

2.1.1. General synthesis of *S*-butyltetrahydrothiophenium bis{(trifluoromethyl)sulfonyl}imide, $[THT_4][TFSI]$, and *S*-(2-methoxyethyl)tetrahydrothiophenium bis{(trifluoromethyl)sulfonyl}imide, $[THT_{G1}][TFSI]$

The alkylating agent, 1-iodobutane (Sigma-Aldrich, 99%, 190.46 g, 1.035 mol, 1.0 eq.) or 2-bromoethyl methyl ether (Fluorochem, 95%, 143.86 g, 1.035 mol, 1.0 eq.), was added to a flask of tetrahydrothiophene (Sigma-Aldrich, 99%, 91.28 g, 1.035 mol, 1.0 eq.) with a small amount of acetone (Sigma-Aldrich, 99.8%). The reaction mixture was stirred vigorously, covered in aluminium foil and left to react for 72 h at 333 K to give the corresponding halide salts as a white solid. After filtration of the solid, each of the intermediate salts were analysed by ^1H NMR. These sulfonium halide salts were then mixed and stirred with a solution of lithium bis{(trifluoromethyl)sulfonyl}imide (3 M, battery grade) (205.84 g,