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Ionic liquids for electrochemical applications: correlation between molecular structure and electrochemical window

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PURPOSE OF THE ABSTRACT

In this work, we studied the correlation between the molecular structure and the electrochemical window (EW) of ionic liquids (ILs) based on ammonium cations.

Over the past decade, ILs have been intensely studied as non-aqueous electrolytes for electrochemical applications, such as transistors [1]. They offer greener technologies with respect to the standard chemicals, allowing better performances.

The main properties of ILs that make them highly interesting and more performant than other types of electrolytes are 1) wide electrochemical windows, that permit to apply of high voltages and obtain an elevated charge accumulation; 2) low melting temperatures or glass transition temperatures, allowing to work in the liquid state at low temperatures reducing the risk of thermal degradation; 3) high conductivities, reducing the charge/discharge time; 4) they are easy to apply as thin layers with a very low thermo-mechanical stress [2].

Despite intensive studies, the correlation between molecular structure and EW is not deeply understood. The problem is that the experiments described in the literature were performed under different conditions, for example, diverse temperatures and electrodes. Therefore, the results are hard to be compared [3].

In this project, a systematic approach was used to understand better how the molecular structure influences the EW. Ammonium based cations were obtained by quaternization of pyrrolidine, piperidine, triethylamine, trimethylamine, dimethylethylamine and diethylmethylamine, adding alkyl chains and ether chains having different lengths (Figure 1).
Bis(trifluoromethanesulfonyl)imide was chosen as anion for its high conductivity and lower hygroscopicity than other anions [4].

The samples were dried and characterized by NMR, IR, and DSC. The samples that showed transition temperatures below -50 °C were also analysed by linear sweep voltammetry to measure the EW. The analysis was performed working with a gold electrode at -33 °C (Figure 2).

The thermal analysis showed that the asymmetric structure of the cation reduced the solidification temperature of the ionic liquids. For certain samples, the glass transition temperature was below -80 °C.

The analysis showed that the EW is enhanced by a balance between the molecular structure of the starting ammine and the length of the chain added by quaternization in the presence or not of oxygen. For certain ionic

liquids, EW of around 5 V was measured.

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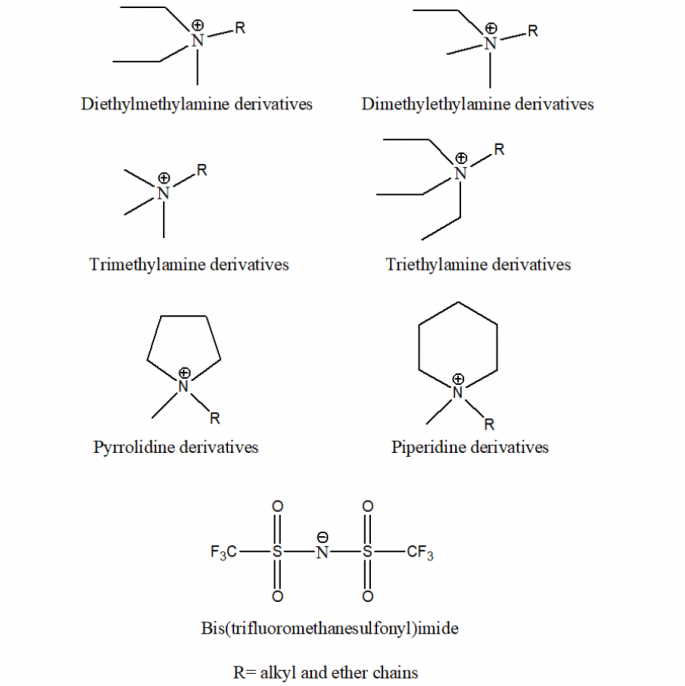
FIGURES



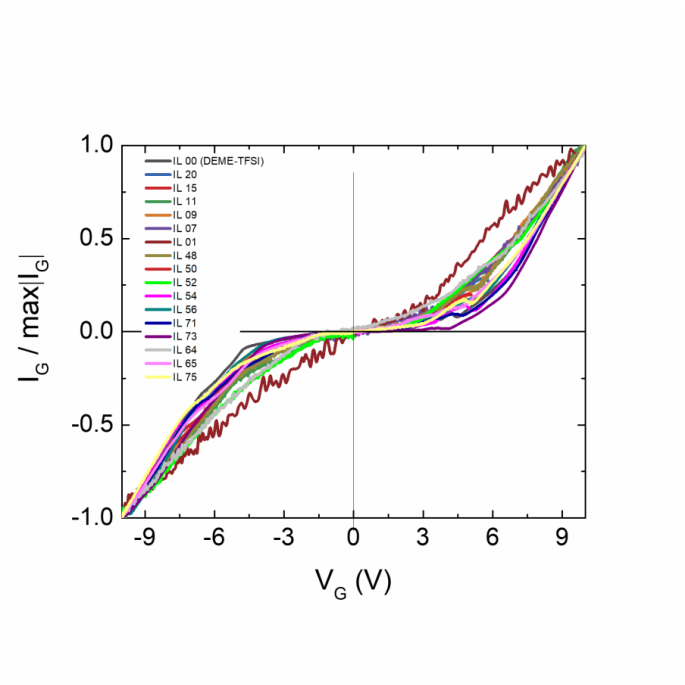


FIGURE 1
Ionic Liquids derivatives studied

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FIGURE 2
Linear-sweep voltammetry of Ionic Liquids

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KEYWORDS
Ionic Liquids | Electrochemistry | Electrochemical window | Molecular structure

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