



## Comparative studies on electrochemical cycling behavior of two different silica-based ionogels



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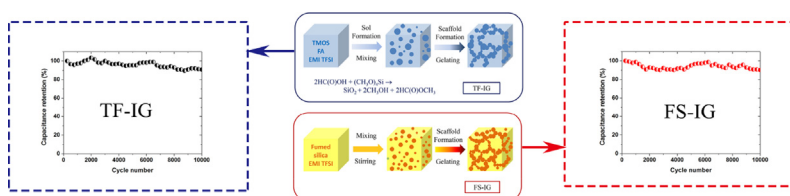
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### HIGHLIGHTS

- A comparative study of two silica-based ionogel electrolytes is reported.
- The electrochemical stability window is reduced with increasing temperature.
- The double layer capacitance is increased with increasing temperature.
- The electrochemical cycling behavior of the two ionogels is excellent.
- 90% capacitance is retained after 10,000 repetitive CV cycles at 100 °C.

### GRAPHICAL ABSTRACT



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### ABSTRACT

We report a comparative study of two silica-based ionogel electrolytes for electrochemical cycling applications. The ionogels considered represent two classes of gel networks, a covalently formed network generated by the polymerization of tetramethoxysilane catalyzed by formic acid, and a network formed by weak intermolecular forces obtained by mixing fumed silica nanopowder with ionic liquid. In both cases, 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide is utilized as the ion conductor in the gel network. With increasing temperature it is shown that the electrochemical stability window is reduced, the conductivity of the electrolyte is increased, and the double layer capacitance is increased for both types of ionogels. Long-term stability of the two ionogels is excellent, with 90% capacitance retained after 10,000 repetitive CV cycles at 100 °C. Our results indicate that both of these ionogel electrolytes are promising for application in solid-state electrochemical systems at high temperature.

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## 1. Introduction

Ionic liquids (ILs) are salts with a melting point below 100 °C or even below room temperature. They are composed of bulky organic

cations and inorganic or organic anions of different sizes. Through the judicious choice of cations and anions, the physicochemical properties of ILs may be tuned, making them an effective solvent for a variety of applications [1]. Ionic liquids have been intensively studied as electrolytes due to their unique combination of properties, such as high ionic conductivity, wide electrochemical stability window (up to 6 V), negligible vapor pressure, non-flammability, and high thermal stability [2,3]. Immobilizing the

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ILs in a solid matrix while keeping their specific properties is an attractive technique for making solid-state electrolytes for all-solid-state electronic devices, sensors and energy harvesting and storage devices. Some examples include dye-sensitized solar cells, electrochromic displays, electrochemical sensors, secondary batteries, fuel cells, and supercapacitors [4–7]. A common method to immobilize ILs is in a flexible gel form, resulting in what is referred to as an ionogel (IG). Two broad classes of ionogels have been reported in the literature. One involves the synthesis of the gel matrix in-situ, where the ionic liquid acts as the solvent for the matrix polymerization reaction [8–12]. The other involves the ionic liquid may be used to swell a pre-formed polymer [13,14] or to impregnate oxide nano-particles [15,16]. Both result in an ionic liquid percolating through a solid network; in the former the network is covalently bound while in the latter the network is held together via weak intermolecular forces.

The present work investigates the electrochemical behavior of two IG materials, based on silica-derived networks, which fall in the two IG classes described above. One gel, covalently bound, is formed by a one-pot sol–gel synthesis of a silica scaffold to immobilize the ionic liquid in situ. In this process, first proposed by Néouze et al. [17,18], the silica scaffold is generated by the polymerization of tetramethoxysilane (TMOS), as catalyzed by formic acid (FA) [19,20]. We refer to this material as TF-IG. The other ionogel is made by mixing fumed silica (FS) nanopowder with ionic liquid to form a gel without any chemical reactions and is held together via weak intermolecular forces [21]. We refer to this material as FS-IG. 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide (EMI TFSI) is utilized as the ionic liquid for both systems because EMI has a high conductivity and reasonably wide electrochemical stability window [22–26]. Although these two silica-based ionogels have been explored before as solid electrolytes [22,27], a detailed comparison of their electrochemical properties has not been reported. We focus this work on a thorough characterization of these materials' electrochemical performance parameters over a range of temperatures relevant to high temperature electrochemical energy storage devices such as supercapacitors, the development of which has recently been a focus of the literature [28]. These devices are specifically attractive for application in power sensors for oil drilling industries, military and space applications. We find that increasing temperature reduces the stable operating potential window while increasing the effective capacitance. High temperature long-term stability characterization is also performed, demonstrating 90% capacitance retention after 10,000 repetitive CV cycles at 100 °C.

## 2. Experimental

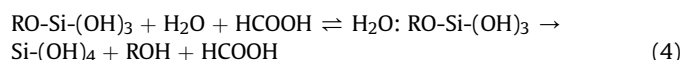
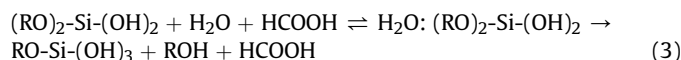
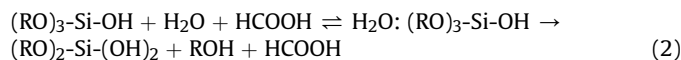
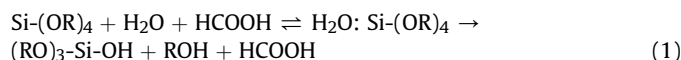
### 2.1. Electrochemical testing cell fabrication

The electrochemical testing cell is fabricated from a Teflon® rod as depicted schematically in Fig. 1. Stainless steel is chosen as the electrode material in order to focus on the behavior of the

electrolyte, rather than that of the electrodes. Stainless steel is electrochemically inert in the examined potential range and hence, is a good test electrode material. Furthermore, a flat electrode is more appropriate than a nanostructured one (e.g., activated carbon) for examining the differences in the electrochemical behavior of the two ionogels at elevated temperatures, which is chosen as the scope of this paper. Stainless steel discs, 3/8" in diameter, are punched out of metal sheets (McMaster Carr). Stainless steel bolts are used to compress stainless steel springs against the electrodes, pinning them against the 1/8" diameter electrolyte reservoir and preventing leakage during the gelation process. A small hole (1/16" in diameter) drilled through the top of the cell allows the electrolyte to be pipetted into the reservoir prior to completion of the gelling process. Cells are filled until slightly overflowing with electrolyte. Electrical contact is made directly through the stainless steel screws.

### 2.2. Ionogel preparation

Fig. 2 schematically shows the mechanisms for the two ionogel formations [29,31]. The TF-IG electrolyte used in this study is prepared as described earlier [28]. First, tetramethoxysilane (99+% purity, Sigma Aldrich), formic acid (97% purity, Alfa Aesar), and EMI TFSI (99% purity, Iolitec) are added in a 1:6:6 M ratio to a glass vial and stirred for ~10 min with a magnetic stir bar. TMOS is used as the precursor to the sol–gel process. FA serves as both solvent and catalyst for hydrolysis and condensation. The hydrolysis process is considered to contain four steps, which are as follows:



where R = CH<sub>3</sub>, H<sup>+</sup> of FA attacks the O of alkoxy in each step. In this

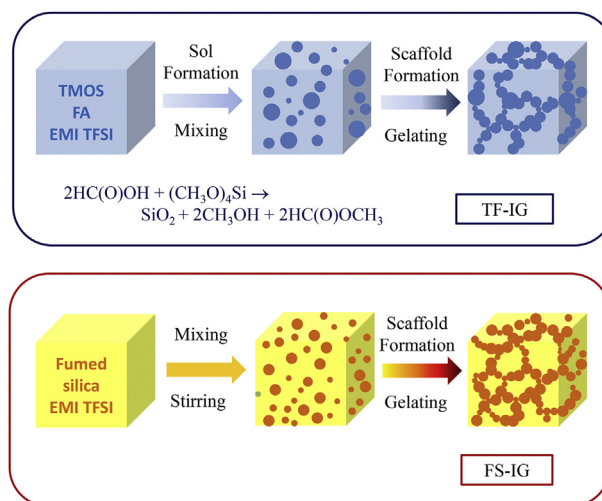


Fig. 2. Possible mechanisms for the formation of the two ionogels. TF-IG represents TMOS + formic acid + EMI TFSI; FS-IG represents fumed silica + EMI TFSI.

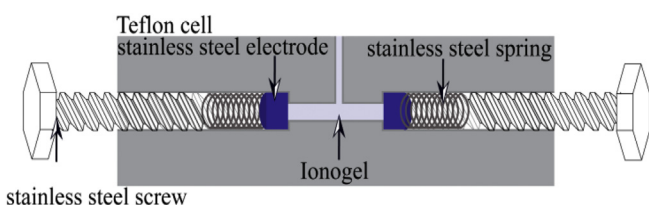


Fig. 1. Depiction of the house made Teflon testing cell.

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