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

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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

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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.

Keyword: ionogel; electrochemical test; long-term stability; high-temperature solid-state electrochemical systems; battery; electrochemical sensor

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 6V), negligible vapor pressure, non-flammability, and high thermal stability.^[2, 3] Immobilizing the 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

Figure 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 molar ratio to a glass vial and stirred for ~10 minutes 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 $\text{R} = \text{CH}_3$, H^+ of FA attacks the O of alkoxy in each step. In this chemical equilibration system, the hydrolysis of the first alkoxy group is a rapid reaction; however, the following hydrolysis reactions are much slower. The key feature of the obtained Si-(OH)_4 is a tendency to condensate:

The hydrolysis and condensation are competing during the sol-gel process, both of which depend on the pH of solvent. Usually, the hydrolysis reaction can be finished in minutes, while the condensation reaction is much slower (hours). Finally, the sol particles aggregate resulting in a 3-D silica scaffold network, in which the ionic liquid is entrapped.^[30]

The second ionogel, FS-IG electrolyte, is prepared by combining fumed silica nanopowder (Sigma-Aldrich, 7 nm) and EMI TFSI in a 0.03:1 mass ratio, which results in a similar ionic liquid weight fraction as TF-IG. The mixture is then stirred for ~2 minutes. The whole process proceeds without any chemical reactions. It is proposed that the hydrophilic nature of fumed silica particles leads to the formation of an extensive 3-D network through aggregation. When ionic liquid is added into this system, hydrogen bonds are formed between the ionic liquid molecules and the -OH groups on the surface of the silica network, producing the ionogel.^[30, 31]

All the samples are prepared in an environmental controlled chamber with N₂ flowing under reduced relative humidity (<1%) to minimize moisture contamination. Both mixtures are transferred via micropipette into the Teflon[®] electrochemical testing cell. The average gelation time of TF-IG is about 21 hours, while FS-IG gelled within 2 hours. The ionogels are allowed to gel for 24 hours prior to electrochemical testing.

2.3 Characterization methods

Electrochemical testing is performed using a potentiostat (CH Instruments, 660D Model). All the samples are kept in a humidity controlled chamber during the

electrochemical testing with relative humidity kept at or below 1%. The stable operating potential window and the specific capacitance are determined by cyclic voltammetry (CV). Various scan rates ranging from 0.02 to 500 V s⁻¹ are applied at room temperature, while 0.05 to 0.1 V s⁻¹ are applied during elevated temperature studies aiming to avoid possible reactions. Galvanostatic charge/discharge cycles are also performed. In order to quantify the equivalent series resistance (ESR), AC impedance spectroscopy with a potential amplitude of 5 mV (frequency range from 0.01 to 10⁶ Hz) is performed. The thermal stability of the two ionogels is probed by thermogravimetric analysis (Thermal Advantage TGA Q50) under nitrogen atmosphere. The samples were heated to 600 °C at a heating rate of 10 °C min⁻¹.

3. Results and discussion

3.1 Electrochemical properties

3.1.1 Cyclic voltammetry

Figure 3 (a) shows the cyclic voltammetry results for a 3.5V potential window at scan rate of 1 V s⁻¹. The CV curves are tilted as has been observed previously for IL electrolyte,^[32-34] with the reasons still under investigation. The electrochemical behavior of the TF-IG differs from that of the FS-IG in three primary ways: the TF-IG shows a higher overall capacitance; it shows symmetric current peaks, and it shows a sharp uptick at 1.5 V, while the FS-IG does not.

The specific capacitance (C) can be calculated via the equation,

$$C = \frac{I_{avg}}{sA} \quad (1)$$

where I_{avg} is the average current magnitude of the cathodic and anodic sweeps, s is the voltage scan rate and A is the total electrode area covered by the ionogel. Figure 3 (b) plots the specific capacitance as a function of scan rate. The capacitance per area measured at 1 V s^{-1} for TF-IG and FS-IG are 14.2 and $5.7 \text{ } \mu\text{F cm}^{-2}$, respectively. These are to be compared to the value of $12.7 \text{ } \mu\text{F cm}^{-2}$ measured for plain ionic liquid, EMI TFSI against a glassy carbon electrode. These values indicate that the inorganic scaffolds of ionogels do not significantly inhibit the capacitive performance of the electrolyte under the probed scan range.

The specific capacitance of both TF-IG and FS-IG drops rapidly with scan rate from 0.02 to 10 V s^{-1} , but then more slowly with the scan rate from 10 to 20 V s^{-1} . This tendency has been observed in our previous work.^[35] The calculated specific capacitance of TF-IG is larger than the FS-IG at low scan rates. This may indicate increased contact area between the entrapped ionic liquid and the electrode in the TF-IG system, whereas the FS-IG system may lead to a physical barrier created by the silica particles decreasing the active electrode area. The higher TF-IG capacitance may also be due to the pseudocapacitive contributions and the sharp uptick at 1.5 V in the TF-IG. This sharp increase in current may indicate electrochemical degradation of the electrode and/or electrolyte and may hence result in an overestimation of real capacitance for the TF-IG. The smaller electrochemical window for the TF-IG may arise from possible reactions between formic acid and stainless steel electrodes. As the scan rate increases, the capacitance values for the two ionogels converge as the

kinetic limitations to the pseudocapacitive and electrochemical degradation contributions are reached.

While these experiments are performed on planar electrodes, we speculate that this difference may be more pronounced on high surface area electrodes, where the fumed silica nanoparticles may inhibit ionic liquid access to small pores, common to supercapacitors. The TF-IG, on the other hand, gels via an in-situ process, which may allow for liquid-phase penetration of electrode pores prior to gelation, as shown via good electrode/electrolyte contact area for FS-IG-based supercapacitors. ^[21] The TF-IG may also slightly increase the capacitance of the system through pseudocapacitance, as evidenced by the symmetric current peaks seen in the CV curve. According to previous research, ^[36] these reactions can contribute to pseudo-capacitance. The nature of these reactions is unclear, as are the reasons why the peaks are observed in the TF-IG but not in the FS-IG. We speculate that excess formic acid may react with the stainless steel electrodes during gelation process and might be responsible for the observed pseudocapacitance.

3.1.2 Galvanostatic charge/discharge

Figure 3 (c) presents representative room temperature galvanostatic charge/discharge curves for the two ionogels at a specific current of $1 \times 10^{-5} \text{ A cm}^{-2}$. Both sets of data include slight curvature at the high end of the potential during charging. These are indicative of irreversible reactions and lead to coulombic efficiencies of 90% and 92% for the FS-IG and TF-IG cells, respectively. The

additional curvature observed in the TF-IG cell charge and discharge curves can be attributed to the pseudocapacitive contributions as discussed in the CV section. The magnitude of the potential drop can be used to estimate the equivalent series resistance (ESR) of the device,^[37] which is calculated to be $258\ \Omega\ \text{cm}^{-2}$ for TF-IG and $426\ \Omega\ \text{cm}^{-2}$ for FS-IG, respectively. The specific capacitance can also be calculated from the charge/discharge curves in the same way as from CV, where the scan rate is replaced with the slope of the discharge curve. The specific capacitance values of TF-IG and FS-IG are 16.4 and $8.3\ \mu\text{F}\ \text{cm}^{-2}$ which are in close accord with the CV results.

3.1.3 AC impedance spectroscopy

Representative AC impedance spectra for the two ionogels are shown in Fig. 3 (d). The equivalent series resistance can be obtained from the x -intercept of the Nyquist plot. The average ESR values of TF-IG and FS-IG are found to be $947\ \Omega\ \text{cm}^{-2}$ and $442\ \Omega\ \text{cm}^{-2}$, respectively. The similar ESR value indicates that ion mobility for these two ionogels is about the same.

3.2 High temperature properties

3.2.1 Thermal stability

The thermogravimetric analysis (TGA) data of the ionogels are shown in Fig. 4. For both ionogels, the weight is almost unchanged until $350\ ^\circ\text{C}$. Above $350\ ^\circ\text{C}$, monotonic decrease in weight loss is observed, similar to the pure EMI TFSI.^[38] The inorganic

scaffold content in the gel can be estimated from the residual weight at 550 °C. The inorganic content of both TF-IG and FS-IG is around 3 %, which is in reasonable agreement with the value of 2.9 %, expected from the starting gel formulation. TGA results confirm that the IL does not contain significant amounts of water or other organic solvents, as well. The data suggest the ionogels are suitable for high temperature energy storage applications, not possible for aqueous (<100 °C) or organic (< 150 °C) based electrolytes.^[39, 40]

3.2.2 Effect of temperature on the electrochemical capacitance

Figure 5 indicates that the potential window shrinks with increasing temperature from room temperature to 200 °C, and symmetric current peaks appear at temperature higher than 100 °C. Therefore, a small potential window of -0.5 V to 0.5 V is used to test all the high temperature electrochemical properties in order to minimize undesired electrochemical reactions. The CV plots of TF-IG and FS-IG are depicted in Fig. 6 (a). The TF-IG still shows a higher overall capacitance, despite the absence of apparent pseudo-capacitive peaks, which implies that the electrode/electrolyte contact area is indeed higher for TF-IG. Figure 6 (b) plots the effect of temperature on the capacitance, showing the capacitance increasing with temperature. A similar behavior has been reported in Ref. [41], in which the capacitance of imidazolium-based ionic liquid increases with temperature. One possible reason is that the ion association decreases with increasing temperature,^[42-44] and thus more ions may be present and get closer to the surface of the electrode at higher temperatures.

3.2.3 Galvanostatic charge/discharge

Figures 7 (a, b) present the galvanostatic charge/discharge curves of the TF-IG and FS-IG at specific current of $5 \times 10^{-5} \text{ A cm}^{-2}$, respectively. Nonlinear discharge curves are observed as temperature increases, resulting from some reactions between electrodes and electrolyte at high temperature. This behavior is in agreement to the results of reduced potential window at higher temperature and the slanted CV at high temperature discussed in the earlier sections.

3.2.4 AC impedance spectroscopy

As previously discussed, the ESR can be obtained from the x -intercept of the Nyquist plot. As shown in Fig. 7 (c,d), the ESR values decrease with increasing temperature. The reasons can be attributed to the increased mobility of ions in the ionogel at elevated temperature.^[29]

3.2.5 High temperature long-term stability

Long-term stability at high temperature is important for electrochemical systems in high temperature applications. A long-term cycling stability test is performed via repetitive CV scans over the full 1V voltage window at a scan rate of 0.1 V s^{-1} at 100°C . Figures 8 (a) and (b) show the percent retained capacitance of TF-IG and FS-IG as a function of the cycle number, respectively. The two ionogels retain 90 % of their initial capacitance after 10,000 cycles, which reveals an excellent stable long-term behavior. A small drop (10 %) in capacitance seen upon cycling is typical of many

supercapacitor devices reported in literature.^[45, 46]

4. Conclusion

In conclusion, both TF-IG and FS-IG ionogel electrolytes are found to be promising as high temperature solid-state electrolyte materials. The electrochemical stability window shrinks from 6V to 1V with increasing temperature, which is attributed to chemical reactions occurring between electrodes and electrolyte at high temperature. Specific capacitance value is on the order of $10^{-5} \text{ F cm}^{-2}$ at room temperature, which increases with increasing temperature. TF-IG possesses slightly higher capacitance comparing with FS-IG, at all temperatures examined, most likely due to increased electrode/electrolyte contact area. Although more data is needed, we speculate that this difference would be magnified for nanoporous electrodes due to the in-situ gelation process of the TF-IG. The ESR values decrease with increasing temperature and become stable at temperature ranging from 100 to 200 °C. Although the CV shape of the TF-IG implies possible instability at room temperature, the high temperature long-term cycling stability of FS-IG and FS-IG is demonstrated, showing that the capacitance retention for both ionogels is about 90% after 10,000 charge/discharge cycles at 100 °C. Although the TF-IG formulation shows higher overall capacitance than the FS-IG, more study of the apparent electrochemical reactions in the TF-IG is needed for device applications. However, this study shows that both of the investigated ionogels hold significant promise for solid-state and high temperature energy storage applications. The expansion of this work to nanostructured electrode

materials is the focus of future work on the device scale.

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Figure(1)

Figure(2)

Figure(3)

Figure(4)

Figure(5)

Figure(6)

Figure(7)

Figure(8)

Captions for Figures

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

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. 3 (a) Cyclic voltammograms of TF-IG and FS-IG at scan rate of 1 V/s, (b) Specific capacitance for both ionogels as a function of scan rate, (c) Galvanostatic charge/discharge curves for the two ionogels at a specific current of $1 \times 10^{-5} \text{ A cm}^{-2}$, (d) AC impedance data showing the Nyquist plot with an enlarged view of the high-frequency region provided in the inset.

Fig. 4 Thermal stability of TF-IG and FS-IG.

Fig. 5 Cyclic voltammograms of FS-IG with scan rate of 50 mV/s at different temperatures.

Fig. 6 (a) Cyclic voltammograms of TF-IG and FS-IG over a 1 V potential window at scan rate of 50mV/s at room temperature, (b) Effect of temperature on the capacitance for scan rate of 50mV/s normalized to capacitance at room temperature, C_0 .

Fig. 7 Galvanostatic charge/discharge curves for (a) TF-IG and (b) FS-IG ionogels at different temperatures, AC impedance spectroscopy of (c) TF-IG and (d) FS-IG at different temperatures.

Fig. 8 Lifetime testing of the ionogels at 100 °C: (a) TF-IG and (b) FS-IG. Capacitance is plotted over 10,000 cyclic voltammetry cycles, normalized by original capacitance value. Scan rate is 0.1 V s^{-1} and voltage window is 1 V.

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