ORIGINAL PAPER

Wanda M. Aylward · Peter G. Pickup

Ion exchange and ion transport properties of sulfonated organically modified silica hydrogels

Abstract Sulfonated ormosil hydrogels ($\sim$80% water) were prepared using tetramethyl orthosilicate as a silica precursor and 2(4-chlorosulfonylphenyl)ethyltrichlorosilane to provide sulfonate functionality for ion-exchange and ion conductivity. Ruthenium(III) hexamine was used as a redox probe in electrochemical studies performed on porous carbon fibre paper electrodes impregnated with the gel. The gel-modified electrodes extracted $Ru(NH_3)_6^{3+}$ from solutions in 0.1 M $CF_3CO_2Na_{(aq)}$ with a partition coefficient of $\sim$36, and with $\sim$100% of the sulfonate sites being accessible for ion exchange. The $Ru(NH_3)_6^{3+/2+}$ couple exhibited reversible and facile electrochemistry in the gel, with a $Ru(NH_3)_6^{2+}$ diffusion coefficient of 4.9×10^{-8} cm^2 s^{-1} determined by chronoamperometry. This is an order of magnitude higher than the mobility of this complex in Nafion. The hydrogel-modified electrodes were stable for days, and could be repeatedly loaded with $Ru(NH_3)_6^{3+}$.

Keywords Hydrogel · Ormosil · Ion exchange · Electrochemistry · Ion transport · Chronoamperometry

Introduction

Recent years have shown rapid advances towards the development of new organic-inorganic micro- and nano-composite materials that combine properties of the individual constituents in a single material [1, 2, 3]. One of the most versatile methods for preparing such composites is based on sol-gel chemistry [4, 5], which allows the synthesis of inorganic materials at low temperatures and avoids any alteration in the functional groups present in the structure.

A wide variety of sol-gel materials have been investigated for electrochemical applications [6, 7, 8, 9], and electrochemical methods have been used to characterise sol-gel processes and the properties of sol-gel materials [10, 11, 12, 13, 14, 15, 16]. Typically, a redox probe is incorporated into the sol-gel matrix and its electrochemistry is monitored. This allows the extraction of information concerning the sol and gel structures, the mobility of entrapped species and extent of intermolecular interactions. Sol-gels can provide both molecular accessibility and rapid mass transport via diffusion because their structures are often composed of three-dimensional networks of nanometer-sized particles surrounded by a continuous mesoporous volume.

The functionalization of sol-gel silicas (organically modified silicas or ormosils), particularly with ionic functional groups, can have pronounced and useful effects on their properties in electrochemical systems. Sulfonated-silica has been demonstrated to have proton conductivity approaching those of the organic proton conducting polymers (like Nafion) used in fuel cells [17]. Silicas with carboxylic and alkylammonium functionality have been shown to exhibit ion-exchange properties and permselectivity [13, 18].

In this paper we report on the synthesis, stability, and ion exchange/transport behaviour of a sulfonated organically modified silica (ormosil) hydrogel derived from tetramethyl orthosilicate and 2(4-chlorosulfonyl phenyl)ethyltrichlorosilane. The ion exchange and ion transport properties of functionalized gels of this type are of fundamental interest and promise applications in diverse applications such as sensors, batteries/supercapacitors, and fuel cells.

W. M. Aylward · P. G. Pickup (✉)
Department of Chemistry,
Memorial University of Newfoundland,
St. John's, Newfoundland, A1B 3X7, Canada
E-mail: ppickup@mun.ca
Tel.: +1-709-7378657
Fax: +1-709-7373702

Experimental

Reagents

Tetramethyl orthosilicate (TMOS, 98%), ruthenium(III) hexaamine chloride, and trifluoroacetic acid (99 + %) were purchased from Aldrich. 2(4-chlorosulfonylphenyl)-ethyltrichlorosilane (50% in CH_2Cl_2) was purchased from United Chem. Technol., Inc., Petrarch Silanes, Silicones and Bonded Silicas. ACS grade methanol and hydrochloric acid were purchased from Fisher. Sodium hydroxide pellets were purchased from EM Science and potassium nitrate (99%) was purchased from BDH Chemicals. All chemicals were used as received. Triply deionised water was used in prepared solutions.

$CF_3CO_2Na_{(aq)}$ solutions were prepared by neutralization of a CF_3CO_2H solution with $NaOH_{(aq)}$. Since it was found that the $Ru(NH_3)_6^{3+/2+}$ redox probe was unstable in the pH = 8 solutions originally prepared, a slight excess of acid was used in all other experiments to give a solution with pH ∼3.3 [19].

Preparation of the hydrogel

A clear and colourless sol was prepared by adding a mixture of 0.6 mL of 2(4-chlorosulfonylphenyl)ethyl-trichlorosilane (50% in CH_2Cl_2) and 2.4 mL of methanol to 1.5 mL TMOS, 1.3 mL deionized water and 0.3 mL 0.1 M HCl in a round bottom flask and heating at reflux for 1.5 h. It was then left in a sealed vial for 1–2 days at ambient temperature to gel. The mass of the mixture typically decreased by 30% during preparation of the gel due to loss of HCl and solvents.

Preparation of modified carbon fibre paper electrodes

Hydrogel modified carbon fibre paper (CFP; Toray-090; thickness 0.28 mm) working electrodes were prepared by suspending strips (∼5.5×30 mm) of CFP in a freshly prepared sol until it became a rubbery hydrogel (1–2 days). Approximately 4 mm of each CFP strip was immersed in the sol. Upon removing the CFP from the gel, excess gel on the surface of the electrode was scraped off. The amount of gel dispersed within the porous carbon matrix was determined from the increase in the mass of the electrode using the density of 1.09 g cm^{-3} determined for a bulk sample of gel.

Electrochemical measurements

Electrochemical measurements were performed at ambient temperature in a conventional glass cell with an Ag/AgCl reference electrode and platinum wire auxiliary electrode. Solutions were purged with nitrogen for fifteen minutes before each experiment.

Results and discussion

Hydrogel and electrode preparation

Hydrogels were prepared by the copolymerization of tetramethyl orthosilicate and 2(4-chlorosulfonylphenyl)ethyltrichlorosilane in a 8.3:1 ratio. As used in the experiments described here, the gel had an initial solvent content (MeOH, H_2O, CH_2Cl_2) of ∼80 mass% and a calculated dry equivalent mass of 733 g/mol SO_3^-. The CH_2Cl_2 (initially ∼5 mass%) was presumably lost during refluxing and gelation, while residual MeOH would be replaced by water during the electrochemical experiments.

In preliminary experiments, films of the gel were prepared on polished glassy carbon disc electrodes by spin coating, and their voltammetry was investigated in a solution of 1 mM $Ru(NH_3)_6^{3+}$ in 0.1 M $KNO_{3(aq)}$. Voltammograms of modified electrodes were not significantly different from those of bare carbon electrodes, and inspection following these experiments revealed that the gel did not stay on the electrode. Use of Triton-X to pretreat the electrode [12] did not help.

In order to produce more stable modified electrodes, the hydrogel was formed within the pores of carbon fibre paper (CFP) electrodes, as described in the "Experimental" section. For ∼4.0 mm×5.5 mm modified electrode areas, this procedure resulted in uptake of an average (for 13 electrodes) mass of hydrogel corresponding to a volume of ∼6.4 ± 0.9 mm^3. This is similar to the void volume of the CFP (4.9 ± 0.2 mm^3 based on 78% porosity [20]), indicating complete filling of the pores with the gel. The slight excess volume of gel relative to the void volume of the CPF is due to residual gel on the surface.

Although the use of three-dimensional gel-impregnated CFP electrodes complicates the electrochemistry, and makes quantitative analysis more difficult and uncertain, it is more relevant to many potential applications than the use of planar glassy carbon electrodes. These applications include sensors [6, 9], fuel cells [21, 22, 23], and batteries/supercapacitors [5, 24], where large active electrode areas and mechanical stability are important.

The gels used in the work reported here were prepared and aged (1–2 days) in closed vials, and therefore contained large volume fractions (∼80%) of solvent. To prevent loss of this solvent, and collapse of the hydrogel structure, the gel-modified CFP electrodes were immersed in electrolyte + redox probe solutions within 3 min of being removed from the vial containing the gel. Aging of the gels for longer periods or exposure to the atmosphere resulted in slow shrinkage due to loss of solvent. The effects of this shrinkage on the ion exchange and ion transport properties of the gel will be the subject of further investigation. In the work reported here, the electrodes were kept wet, except for superficial drying for ∼5 min during transfer between solutions. No

changes were observed in the properties of the gels during the experiments, and so it would appear that the gels maintained their open, porous structures over the multi-day experiments.

Ion-exchange and stability

Figure 1 shows cyclic voltammograms for bare and gel-modified CPF electrodes in 0.1 M $KNO_{3(aq)}$ containing $Ru(NH_3)_6^{3+}$. The $Ru(NH_3)_6^{3+/2+}$ electrochemistry was reversible at the gel-modified electrode and peak currents were much larger than observed at the bare electrode, indicating that $Ru(NH_3)_6^{3+}$ became concentrated in the gel by ion-exchange. The $Ru(NH_3)_6^{3+/2+}$ waves at the gel-modified electrode increased with time for ~5 h, and were then stable for at least another hour. In longer term experiments it was found that the $Ru(NH_3)_6^{3+}$ in 0.1 M $KNO_{3(aq)}$ solution was unstable, and so further experiments were conducted with CF_3CO_2Na [19] as the supporting electrolyte.

Figure 2 shows voltammograms, in a solution containing no $Ru(NH_3)_6^{3+}$, of a gel-modified electrode that had been pre-loaded with $Ru(NH_3)_6^{3+}$ by soaking it in a 1 mM $Ru(NH_3)_6^{3+}$ + 0.1 M $CF_3CO_2Na_{(aq)}$ solution for 24 h. Again, large reversible $Ru(NH_3)_6^{3+/2+}$ waves were seen, indicating concentration of $Ru(NH_3)_6^{3+}$ in the gel by ion-exchange. These waves decreased in height over a period of ~3 h, as the new ion-exchange equilibrium was established, and then remained stable for at least two more hours.

Voltammograms like those shown in Figs. 1 and 2 exhibited a linear relationship between peak currents and square root of scan rate (not shown), indicating diffusion control of the current. Therefore the charges under the voltammograms do not allow estimation of the concentration of $Ru(NH_3)_6^{3+}$ in the gel, even at scan

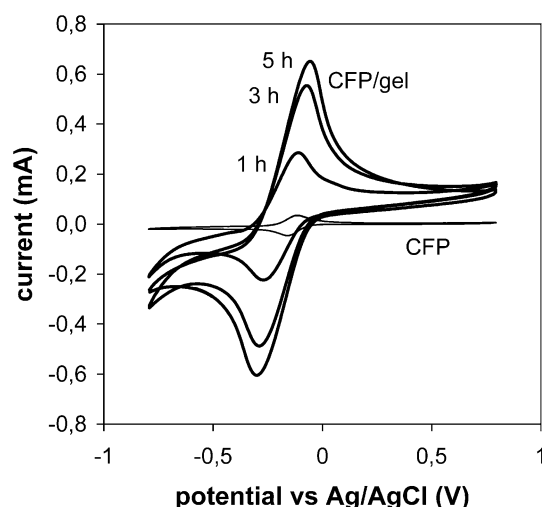**Fig. 2** Cyclic voltammograms (10 mV s^{-1}) of a $Ru(NH_3)_6^{3+}$ loaded (1 mM; 24 h) CFP/gel electrode in 0.1 M $CF_3CO_2Na_{(aq)}$. The initial three scans are shown, together with a steady state voltammogram (bold) recorded after 5 h

rates as low as 1 mV s^{-1}. This is primarily a consequence of the thickness of the gel layer. Concentrations and partition coefficients were therefore determined by chronocoulometry (see below).

The larger than theoretical (59 mV) peak separations observed in Figs. 1 and 2 are due to the uncompensated solution resistance. This has a pronounced effect here because of the high currents generated by the three-dimensional CFP/gel electrode, relative to a planar modified electrode. In order to demonstrate and minimize the effect of the solution resistance, the concentration of the supporting electrolyte, CF_3CO_2Na, was increased to 1 M. This decreased the peak separation, but led to excessive leaching of $Ru(NH_3)_6^{3+}$ from the gel (Fig. 3). The peak current decreased to half of its ori-

Fig. 1 Cyclic voltammograms (10 mV s^{-1}) of gel loaded and bare CFP electrodes in 0.1 M $KNO_{3(aq)}$ containing 1 mM $Ru(NH_3)_6^{3+}$. Voltammograms at ~1 h, 3 h, and 5 h in the solution are shown for the gel electrode

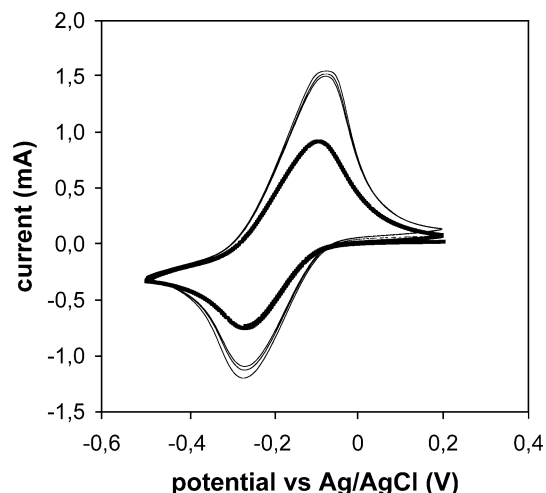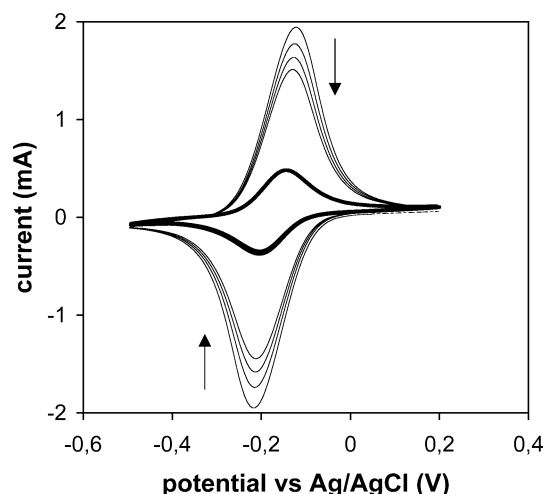**Fig. 3** Cyclic voltammograms (10 mV s^{-1}) of a $Ru(NH_3)_6^{3+}$ loaded (1 mM; 24 h) CFP/gel electrode in 1 M $CF_3CO_2Na_{(aq)}$. The initial four scans are shown, together with a voltammogram (bold) recorded after 75 min
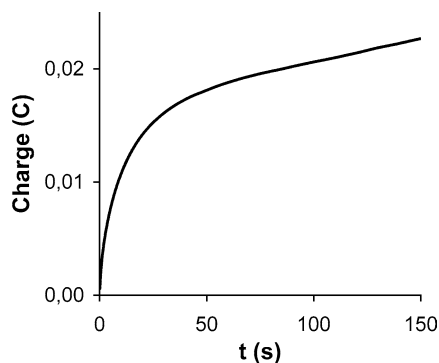
Fig. 4 Chronocoulometric plot for a −0.4 to +0.2 V potential step on a Ru(NH$_3$)$_6^{3+}$ loaded (1 mM; 24 h) CFP/gel electrode in 0.1 M CF$_3$CO$_2$Na$_{(aq)}$. Data for the same experiment on a bare CPF electrode have been subtracted as a background correction

ginal value in only 15 min, and continued to decrease with time.

The pH of the electrolyte solution was also found to strongly influence the voltammetric behaviour of the Ru(NH$_3$)$_6^{3+}$-loaded CFP/gel electrodes. The results shown in Figs. 2 and 3 were obtained with a slightly acidic (pH~3.3) CF$_3$CO$_2$Na electrolyte. When a higher pH(~8) solution was used, the characteristic Ru(NH$_3$)$_6^{3+/2+}$ peaks were absent.

The gel modified electrodes showed no deterioration over several days of use and could be reloaded with Ru(NH$_3$)$_6^{3+}$ following leaching and reused.

Partition coefficients

Concentrations of Ru(NH$_3$)$_6^{3+}$ in gels that had been equilibrated in solutions containing various concentrations of Ru(NH$_3$)$_6^{3+}$ in 0.1 M CF$_3$COONa were determined from the limiting charge values obtained from chronocoulometry in 0.1 M CF$_3$COONa containing no Ru(NH$_3$)$_6^{3+}$. Figure 4 shows a typical charge versus time plot. Although these data have been corrected by subtraction of the background currents measured at a bare electrode, the charge continues to rise linearly at long times, indicating the presence of addition background currents. These may be due to Ru(NH$_3$)$_6^{2+}$ that is either in dense poorly accessible regions of the gel, or the bulk solution. In order to estimate the concen-

tration of Ru(NH$_3$)$_6^{2+}$ in the gel available for facile electrochemistry, this contribution to the final charge was neglected. This is the most appropriate concentration to use in kinetic analyses (see below) but it may underestimate partition coefficients by ~20–30%.

Table 1 shows partition coefficients ($K_P =$ [Ru(NH$_3$)$_6^{3+}$]$_{gel}$/[Ru(NH$_3$)$_6^{3+}$]$_{solution}$) for Ru(NH$_3$)$_6^{3+}$ in the gel. Over the range of solution concentrations studied, the concentration of Ru(NH$_3$)$_6^{3+}$ in the gel increased approximately linearly with increasing solution concentration. The partition coefficient was 36 ± 8.

The concentration of sulfonate groups in the gel can be estimated to be ~0.3 M based on the mass and approximate composition of the gel. This is only three times the maximum Ru(NH$_3$)$_6^{3+}$ concentration of 0.10 M reported in Table 1, indicating that essentially all of the sulfonate sites are associated with the Ru complex at the highest loading used.

Diffusion coefficients for Ru(NH$_3$)$_6^{3+/2+}$ in the gel

The Faradaic current that flows when a redox species undergoes reversible electron-transfer at an electrode provides a direct measure of the apparent diffusion coefficient (D_{app}) of the redox species [25]. This can best be determined from chronoamperometry (or chronocoulometry for a planar electrode). Figure 5 shows a typical chronoamperometry (Cottrell) plot obtained for a Ru(NH$_3$)$_6^{3+}$-loaded CFP/gel electrode in 0.1 M CF$_3$COONa when stepped from −0.4 V to 0.2 V. The current at the shortest times is limited by the solution resistance, but then there is a linear i versus $t^{-1/2}$ region that appears to fit the Cottrell equation. At long times, the current falls sharply due to depletion of Ru(NH$_3$)$_6^{2+}$ within the finite volume of gel. Application of the Cottrell equation to the intermediate linear region gave a D_{app} value of ~1×10^{-7} cm^2 s^{-1}, which would correspond to a diffusion layer thickness of ~4.5 μm at $t = 1$ s. Since this is much larger than 10% of the radius (4.2 μm determined by SEM) of the fibres of the CPF, the use of the Cottrell equation, which assumes linear diffusion, is invalid [25]. The Cottrell equation is only valid for times up to ~10 ms, and at such short times, the current is limited by the solution resistance.

Table 1 Partition coefficients for Ru(NH$_3$)$_6^{3+}$ and diffusion coefficients for Ru(NH$_3$)$_6^{2+}$ in gels loaded from different concentrations of Ru(NH$_3$)$_6^{3+}$ in 0.1 M CF$_3$CO$_2$Na$_{(aq)}$

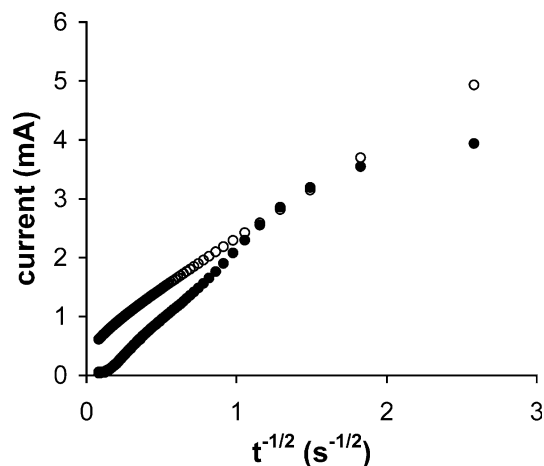| [Ru(NH$_3$)$_6^{3+}$]$_{soln}$ (mM)	[Ru(NH$_3$)$_6^{3+}$]$_{gel}$ (mM)	K_p	D_{2+} (10^{-8} cm^2 s^{-1})
0.5	12.7	25.3	11
1.00	22.8	22.8	5.2
1.21	30.8	25.5	4.0
1.42	42.4	29.9	4.2
1.50	44.6	29.8	5.1
1.94[a]	96.5, 99.3	49.7, 51.1	4.5, 3.8
2.00[a]	78.3, 80.0	39.2, 40.0	4.1, 4.2
2.45[a]	92.2, 94.0	37.6, 38.4	5.3, 4.1
2.97[a]	102, 104	34.2, 34.9	4.0, 3.9

[a] Duplicate measurements

Fig. 5 Chronoamperometric plot (filled dots) for a −0.4 to +0.2 V potential step on a $Ru(NH_3)_6^{3+}$ loaded (1 mM; 24 h) CFP/gel electrode in 0.1 M $CF_3CO_2Na_{(aq)}$. Unfilled dots are data calculated from Eq. 1

The chronamperometric response for diffusion to a cylindrical microelectrode of radius r can be represented by the following equation [25]:

$$i = \left(nFAD_{app}C/r\right)\left[2\exp\left[-0.05\pi^{3/2}\tau^{1/2}\right]/\pi^{1/2}\tau^{1/2} + 1/\ln\left(5.2945 + 0.7493\tau^{1/2}\right)\right] \quad (1)$$

where $\tau = 4D_{app}t/r^2$, C is the concentration of $Ru(NH_3)_6^{2+}$ in the gel (Table 1), and A is the total area of the fibres. An average area of 5.3 ± 0.2 cm^2 was calculated from r and the total volume of the carbon fibres (electrode volume×(1−porosity)). D_{app} can be obtained by manual fitting of this equation to the experimental data at short times (Fig. 5). At longer times (>1 s), the finite distance between fibres leads to more rapid depletion of $Ru(NH_3)_6^{2+}$ than predicted by the semi-infinite diffusion assumption implicit in Eq. 1, and the experimental current falls below the calculated current.

The apparent diffusion coefficients (D_{app}) for the ruthenium complex in the gel modified electrode, as determined from Eq. 1, were 5.2×10^{-8} cm^2 s^{-1} for the $Ru(NH_3)_6^{2+}$ ion (−0.4 to 0.2 V step) and 2.4×10^{-8} cm^2 s^{-1} for $Ru(NH_3)_6^{3+}$ (0.2 to −0.4 V step). The larger D_{app} for the less highly charged ion indicates dominance by molecular diffusion, rather than electron hopping [19]. Similar behaviour was reported by Buttry and Anson [19, 26] for $Ru(NH_3)_6^{3+/2+}$ in Nafion films coated on pyrolytic graphite electrodes. They believed that the diffusion of this complex proceeded by physical motion, thereby giving two distinct D_{app} values because of the different charge size ratios of the 2+ and 3+ ions [19].

Measured values of D_{app} for the $Ru(NH_3)_6^{2+}$ probe in the gel were independent of probe concentration in the gel over the range of 10–100 mM, as shown in Table 1. The average was $(4.9\pm1.9)\times10^{-8}$ cm^2 s^{-1}. This again suggests that electron hopping does not contribute significantly to D_{app}.

The D_{app} values reported here are quite low relative to the values of 10^{-7} to $>10^{-6}$ cm^2 s^{-1} reported for various species in unmodified silica hydrogels [14, 15]. Clearly, electrostatic interactions with the immobilized sulfonate groups greatly restrict the mobility of the Ru complex, as is found in ion-exchange polymers such as Nafion ($D_{app}\sim2\times10^{-9}$ cm^2 s^{-1} [26]).

All D_{app} values reported here were determined using the concentrations reported in Table 1, which represent average values for the whole gel volume. Any shrinkage of the gel during the experiments or exclusion of the complex from certain regions of the gel would mean that the real concentrations were higher, and the D_{app} values would be correspondingly lower. This has been observed for bulk silica hydrogels using a microdisc electrode, which allows simultaneous determination of C and D_{app} [14, 15].

Conclusions

Ormosil hydrogels formed from tetramethyl orthosilicate and 2(4-chlorosulfonylphenyl)-ethyltrichlorosilane in a 8.3:1 ratio exhibited excellent ion exchange and ion transport properties, and were very stable in electrochemical studies. Cyclic voltammetry with $Ru(NH_3)_6^{3+/2+}$ as a redox probe showed reversible behaviour of the probe in the gel matrix. Gel-modified carbon fibre paper electrodes did not show any deterioration over a period of days in the electrolyte solution.

$Ru(NH_3)_6^{3+}$ partitioned strongly into the gel ($K_p\sim36$) with essentially all of the gel's sulfonate sites being available for ion exchange. The ion exchange process was facile and could be reversed by immersing the gel in a concentrated electrolyte solution containing no $Ru(NH_3)_6^{3+}$. Electrodes could be reloaded and re-used. The diffusion coefficients for the redox probe ions in the gel were high (4.9×10^{-8} cm^2 s^{-1} for $Ru(NH_3)_6^{2+}$) for an ion-exchanger, indicating that the gel had a well hydrated and open structure.

The significance of these results can be illustrated by a comparison with Nafion, in which $Ru(NH_3)_6^{3+/2+}$ exhibits a D_{app} value of only $\sim2\times10^{-9}$ cm^2 s^{-1} [26]. Nafion has an equivalent mass of ~1100 g/mol SO_3^- and a hydration level of $\sim30\%$, while the gel reported here had an equivalent mass of 733 g/mol SO_3^- and a hydration level of $\sim80\%$. The gel is clearly a superior matrix for ion transport, and our initial assessment of its stability is very encouraging for such a porous material. Supporting the gel within a carbon fibre matrix is an important aspect of its stability. Further work is needed to probe the evolution of the gel's properties and the integrity of the CFP modified electrodes as the gel dries, and to find appropriate drying procedures to maintain the integrity of the gel.

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