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Ion Transport in Sulfonated Nanoporous Colloidal Films

Joanna J. Smith and Ilya Zharov*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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The surface of self-assembled nanoporous silica colloidal crystalline films comprised of 184-nm-diameter silica spheres has been sulfonated using 1,3-propanesultone. The transport of ions through the sulfonated films has been studied using cyclic voltammetry in water as a function of ion charge, pH, and solution ionic strength. We found that the flux of anions through the sulfonated colloidal films is reduced, while the flux of cations is increased, compared to the unmodified colloidal films. This behavior is pH-dependent and is due to electrostatic repulsion/attraction that can be modulated by changing the ionic strength of the contacting solution.

Introduction

There is a growing interest in nanoporous materials,[1,2] with applications in separations, drug release, and fuel cells. Silica colloidal crystals are promising candidates for such materials, because they form via self-assembly,[3] contain ordered arrays of three-dimensional interconnected nanopores, and are characterized by a diffusive flux that is only ca. 10 times smaller relative to the free solution value, independent of the size of the nanopores.[4] In addition, the surface modification of the silica colloidal crystals is facile.[5,6] The potential of colloidal crystals as separations media has been recognized by several research groups.[7−11]

Recently, we reported ion and molecular transport studies in amine-modified colloidal films,[12,13] in colloidal films surface-modified with chiral selector moieties[14,15] and polymer brushes,[16,17] and in suspended colloidal crystals.[18]

In a continued effort to investigate the ion transport through surface-modified colloidal nanopores, we prepared and studied colloidal films carrying surface-bound sulfonic groups. We expected that such groups would introduce a permanent negative charge to the colloidal surface, as opposed to the negative charge of unmodified silica surface, which is significant only at relatively high pH.[19,20] In the present report, we describe the transport of

Scheme 1
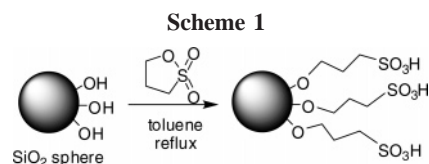
both cations and anions through the sulfonated colloidal films in terms of electrostatic attraction/repulsion and investigate the transport mechanism.

Experimental Section

Materials. Hexaamineruthenium(III) chloride, $Ru(NH_3)_6Cl_3$ (99%, Strem Chemicals), potassium chloride (99%, Mallinckrodt), potassium hexachloroiridate(III), K_3IrCl_6 (98%, Aldrich), 1,1′-ferrocene-dimethanol [$Fc(CH_2OH)_2$, 98%, Aldrich], and 1,3-propanesultone (99+%, Aldrich) were used as received.

Sulfonation of Silica Spheres. Silica spheres were synthesized[21−24] by adding 0.2 M tetraethyl orthosilicate (TEOS) in absolute ethanol to a solution of 0.4 M ammonia and 17 M water in absolute ethanol. The mixture was stirred for 24 h at room temperature. Silica spheres were collected and purified by repeated centrifugation in absolute ethanol. The diameter of the spheres was determined to be 184 ± 9 nm using SEM.

The sulfonation of the silica spheres was conducted using the reaction shown in Scheme 1. Silica spheres (6 g) were suspended in 600 mL of 0.1 M toluene solution of 1,3-propanesultone and the colloidal solution was refluxed for 48 h. The sulfonated spheres were isolated and purified by repeated washing and centrifugation.

Pt Microdisk Electrodes. Pt microdisk electrodes (25 μm in diameter) shrouded in glass were prepared by first attaching a 1.0 mm diameter Cu wire (Alfa Aesar) to a 25 μm diameter Pt wire using Ag paint (DuPont). The Pt wire was then flame-sealed in a glass capillary; the capillary was bent to a U-shape and the end cut orthogonal to the length of the capillary with a diamond saw to expose the Pt disk. The resulting electrodes were then polished with microcut paper disks (Buehler), from 240 to 1200 grit in succession, until the surface was free from visible defects.

Sulfonation of Colloidal Films. Colloidal films were assembled on the electrode surfaces by placing the electrodes vertically[25] in a 1.5 wt % colloidal solution of the silica spheres in ethanol and

* To whom all correspondence should be addressed. E-mail: i.zharov@utah.edu.

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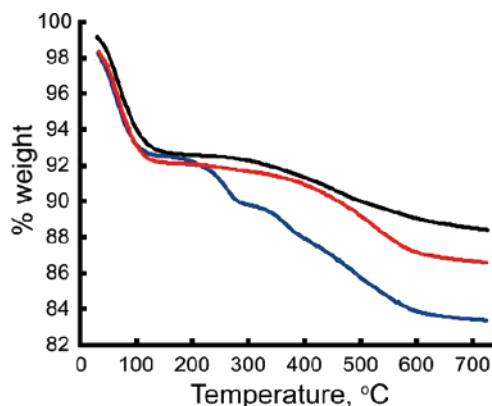
Figure 1. Thermogravimetric analysis (TGA) for the unmodified (black) and sulfonated silica spheres purified with ethanol (blue) and water (red).

letting the solvent evaporate for 2−3 days in a vibration-free environment. This resulted in 6.5-μm-thick films.

The surface of the spheres, after assembly into colloidal films on the Pt electrode, was modified with sulfonic acid groups by immersing the electrode under nitrogen in refluxing toluene containing 0.06 M of 1,3-propanesultone for 48 h. After modification, the electrodes were soaked and rinsed in toluene, acetonitrile, and water. Representative images (top and side view) of a sulfonated colloidal film are shown in Figure 3.

Voltammetric Measurements. The flux of permeants across the colloidal film was measured voltammetrically using a two-electrode cell and an Ag/AgCl reference/counter electrode. A Par Model 175 Universal Programmer and Dagan Cornerstone Chem-Clamp potentiostat were used to conduct the measurements. Data were recorded with a PC using programs written in LabView. Aqueous solutions were prepared using 18 M$\Omega\cdot$cm water obtained from a Barnstead "E-pure" water purification system. All solutions were purged with N_2 to remove dissolved O_2. pH was adjusted by the addition of sulfuric acid and sodium hydroxide. The following concentrations of redox species were used: 5.0 mM $Ru(NH_3)_6^{3+}$, 1.6 mM $Fc(CH_2OH)_2$, and 2.0 mM $IrCl_6^{3-}$.

Characterization. Dynamic light scattering (Brookhaven Zeta-PALS) was employed to measure size and ζ-potential of unmodified and sulfonated silica spheres. To characterize the surface composition of the silica spheres, X-ray photoelectron spectroscopy (XPS) analysis (Kratos Axis Ultra DLD), Raman spectroscopy (PI-200 Raman Analyzer, Process Instruments), and thermogravimetric (TGA) analysis (TGA Q500, TA Instruments) were performed. Scanning electron microscopy (Hitachi S3000-N) was used to image the sulfonated colloidal films.

Results and Discussion

Sulfonation of Silica Spheres. The silica sphere surface was sulfonated following a well-established procedure[26−28] using 1,3-propanesultone in refluxing toluene (Scheme 1). To confirm the surface modification of the silica spheres, we performed a TGA analysis for the predried sulfonated silica spheres and compared it to the TGA of the unmodified spheres (Figure 1). To eliminate the possibility of physisorption of the sulfonic acid species on the silica surface, the modified silica spheres were extensively purified by washing and centrifugation, first in acetonitrile and then in water. Interestingly, the behavior of the sulfonated silica spheres in the TGA experiment was dependent on the solvent used for the purification, as shown in Figure 1. The TGA plots show a major weight loss below 150 °C, attributed to strongly adsorbed water on the hydrophilic silica spheres surfaces. In

contrast to a smooth weight loss in the unmodified sample due to the silica sphere drying, we observed a significant weight loss for the sulfonated spheres between 300 and 600 °C. Such behavior has been attributed earlier to the loss of the hydrated propane-sulfonate moieties from silica surfaces.[29−32] However, the amount of the weight loss for the sulfonated silica spheres washed with acetonitrile was much greater compared to that for the sulfonated silica spheres washed with water. To eliminate the possibility that this behavior results from hydrolysis, we compared the TGA of the sulfonated silica spheres washed with water for 5 min and for 10 h. Both samples produced identical TGAs. These observations suggest that washing the sulfonated silica spheres with acetonitrile does not remove water-soluble byproducts of the sulfonation reaction.

Thus, we used the TGA results for the water-purified sulfonated silica spheres to estimate the surface density of the sulfonic groups, especially since the ion transport measurements (see below) have been conducted in water. Using the geometrical surface calculated on the basis of the silica sphere diameter, we obtained the surface density of sulfonic groups as 5.5 group/nm². This number is slightly higher than that expected for complete monolayer coverage of silica surface (based on a typical ∼4 groups/nm² density of hydroxyl groups on silica surface[33]). It may result from sulfonic groups being hydrated even under the dry conditions, as has been observed for other polysulfonated materials.[34] Assuming a degree of sulfonation of 4 group/nm² for the silica spheres leads to an estimate of 2.6 molecules of water per sulfonic group. The second factor that may have contributed to the higher than expected degree of sulfonation is the surface porosity. However, it has been shown that silica spheres prepared by the Stöber method have low porosity and their surface area is only moderately underestimated by the geometrical calculation.[35]

To further confirm the attachment of propanesulfonic acid moieties to the silica surface, the presence of sulfur atoms on the surface of the dried water-purified silica spheres has been examined by X-ray photoelectron spectroscopy (XPS). The sulfur atom peak in the XPS spectra of the sulfonated silica spheres was found at 166 eV, which can be attributed to sulfur atoms in sulfonic acid groups.[28] In addition, an increase in the O/Si atomic concentration ratio has been observed after the sulfonation. Furthermore, Raman spectra were obtained for both dried water-purified sulfonated and unmodified silica spheres. The Raman spectra of the modified spheres showed a strong band at 1048 cm^{-1}, which is characteristic of the SO_3H groups.[36] This band was not present in the unmodified sample.

To investigate the effect of sulfonation on the surface charge of the silica spheres, ζ-potentials of unmodified and sulfonated silica spheres have been compared (Figure 2). Because ζ-potentials are highly dependent on solution ionic strength,[37] we conducted ζ-potential measurements in 0.03 M solutions of KCl to maintain constant ionic strength. This resulted in overall low ζ-potential values that still clearly show the difference between the unmodified and sulfonated spheres. Indeed, at pH ∼ 2−3, the unmodified silica spheres showed ζ-potential of ca. 0 mV,

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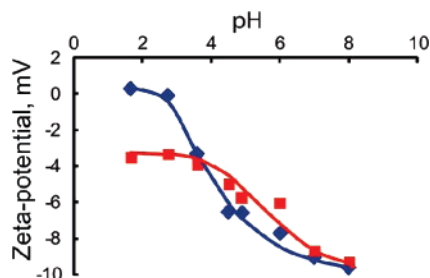
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Figure 2. ζ-Potential for unmodified (blue) and sulfonated (red) silica spheres in 0.03 M aqueous KCl as a function of pH.
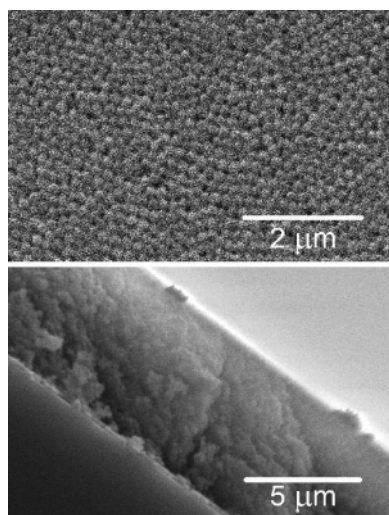

Figure 3. SEM images of the sulfonated colloidal film prepared from 184-nm-diameter silica spheres: (A) top view and (B) side view.

while the sulfonated silica spheres were more negatively charged (-4 mV). The ζ-potential for both types of silica spheres increased with increasing pH and reached ca. -10 mV for both sphere types. The behavior of the sulfonated and unmodified silica spheres parallels that reported earlier.[19,20,38]

Observations described above clearly demonstrate the presence of sulfonic acid groups covalently attached to the silica sphere surfaces and a high degree of surface sulfonation.

Effect of Colloidal Film Sulfonation on the Molecular Flux. In order to examine the effect of surface sulfonation on the transport of charged species through the colloidal films, we measured the voltammetric responses of 25-μm-diameter Pt microdisk electrodes in aqueous solutions carrying a sulfonated colloidal film of ca. 35 layers, which is approximately equal to 184 nm silica spheres. To prepare sulfonated colloidal films on the glass-shrouded Pt microelectrodes, the films were assembled using unmodified silica spheres and sulfonated by immersing the electrodes in refluxing toluene containing 1,3-propanesultone, followed by rinsing with acetonitrile and water. A representative image of the sulfonated colloidal film is shown in Figure 3. It is clear that the colloidal crystalline lattice remained mostly intact, although it appears that some silica spheres have been removed from the top colloidal film layer during the sulfonation process.

Three redox couples have been studied: a multiply charged anion, $IrCl_6^{3-}$; a multiply charged cation, $Ru(NH_3)_6^{3+}$; and a neutral molecule, ferrocenedimethanol, $Fc(CH_2OH)_2$. The voltammetric responses for each redox couple in the case of the bare electrodes showed a sigmoidal shape (Figure 4) characteristic of

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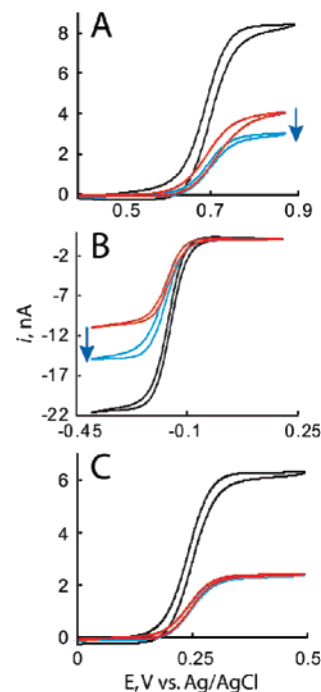

Figure 4. Representative voltammetric responses of bare electrodes (black) and colloidal film electrodes before (red) and after (blue) silica surface sulfonation for (A) $IrCl_6^{3-}$, (B) $Ru(NH_3)_6^{3+}$, and (C) $Fc(CH_2OH)_2$ at neutral pH with 0.1 M aqueous KCl. The decrease (A) and increase (B) in the limiting current is shown with arrows.

near steady-state radial diffusion of the redox species to a microelectrode.[39] Following deposition of the thin silica colloidal film onto the electrodes, a near steady-state radial diffusion with a $\sim$60% reduction in the limiting current (i_{lim}) was observed, in agreement with our previous observations[12,13] and with finite-element simulations of the quasiradial flux of redox species to a disk-shaped microelectrode coated with a colloidal film, reported earlier.[13]

The effect of the surface sulfonation is readily apparent in the voltammetric response of the electrode after the covalent attachment of sulfonic acid groups to the silica spheres. Indeed, compared to the unmodified colloidal film electrodes, for the sulfonated colloidal films the voltammetric limiting current (i_{lim}) corresponding to the one-electron oxidation of $IrCl_6^{3-}$ is diminished (Figure 4A), and i_{lim} corresponding to the one-electron reduction of $Ru(NH_3)_6^{3+}$ is increased (Figure 4B), while i_{lim} for the one-electron oxidations of $Fc(CH_2OH)_2$ remains the same as before the surface modification (Figure 4C). This result is consistent with electrostatic attraction of the cationic species, $Ru(NH_3)_6^{3+}$, and electrostatic repulsion of the anionic species, $IrCl_6^{3-}$, by the negatively charged sulfonated surface. These results have been reproduced on seven sulfonated colloidal film electrodes, with the limiting current drop of 19 ± 8% observed for $IrCl_6^{3-}$ and the limiting current increase of 21 ± 12% for $Ru(NH_3)_6^{3+}$.

The above observations are similar to those reported by us earlier[12,13] for positively charged protonated amine-modified colloidal films, where the transport of the positively charged species was blocked. However, in the latter case, a more complete blockage of the transport has been observed. We believe that this may be the result of three factors: (i) having a thin polymeric film with multiple layers of amino groups in the case of the aminated colloidal films,[13] as compared to a monolayer of sulfonic

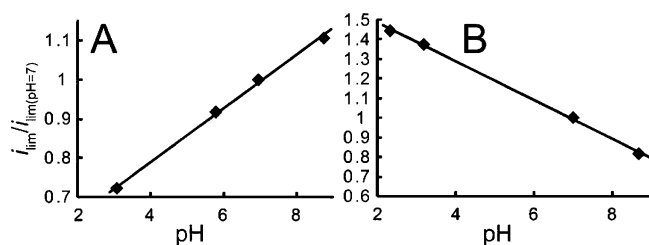(39) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Wiley: New York, 2001.

Figure 5. Relative limiting current of the sulfonated colloidal film electrodes as a function of pH for $Ru(NH_3)_6^{3+}$ (A) and for $IrCl_6^{3-}$ (B).

Figure 6. Relative limiting current of the sulfonated colloidal film electrodes as a function of KCl concentration for $Ru(NH_3)_6^{3+}$ (A) and for $IrCl_6^{3-}$ (B).

acid groups; (ii) conducting the experiments described above at a relatively high ionic strength of the contacting solution, which would further diminish the electrostatic effect (see below); and (iii) comparing the transport through the sulfonated colloidal films to that through the unmodified silica colloidal films that carry a surface negative charge as well (see below).

To verify that the observed behavior results from the surface modification of the colloidal film and not of the Pt electrode surface, we treated the bare Pt electrodes with 1,3-propanesultone in refluxing toluene. The treated electrodes did not show any difference in response to positively or negatively charged redox species.

pH Effect on Diffusion through Sulfonated Colloidal Films. The effects of the surface sulfonation on the molecular transport rates through the colloidal films described above have been observed at neutral pH, where both unmodified and sulfonated silica surface are expected to possess a negative charge. Thus, these effects demonstrate the increase in the electrostatic effects as a result of the sulfonation. The effects are relatively modest, suggesting that the negative charge on the silica surface at pH 7 does not increase dramatically as a result of the sulfonation. This is reflected in qualitatively similar ζ-potentials of the unmodified and sulfonated silica spheres at neutral pH (Figure 2), although we were unable to find a suitable approximation to accurately calculate the surface charge density for the sulfonated silica spheres based on these data.[40]

Decreasing pH should lead to the protonation of the sulfonic groups and to a further decrease in the electrostatic potential inside the nanopores. In order to examine the effect of pH on transport rates, we measured the limiting current of the sulfonated colloidal film electrodes for $Ru(NH_3)_6^{3+}$ and for $IrCl_6^{3-}$ between pH 9 and 2 (Figure 5). We found that the diffusion of the positively charged species across the sulfonated colloidal film is decelerated by decreasing the pH of the contacting solution (Figure 5A), which is likely the result of the protonation of the surface sulfonic groups. In contrast, the flux of $IrCl_6^{3-}$ increases as the pH of the contacting solution is decreased (Figure 5B). In both cases, the dependence of i_{lim} on pH is linear, but the magnitude of the effect is slightly different for $Ru(NH_3)_6^{3+}$ (a slope of 0.07) and for $IrCl_6^{3-}$ (a slope of −0.1). For comparison, we performed analogous measurements for a neutral molecule, ferrocenedimethanol, and found no pH dependence for its flux across the sulfonated colloidal film (Figure SI1).

The dependence of i_{lim} on pH for the sulfonated colloidal films is different compared to that of the amine-modified colloidal films, where a sigmoidal-shaped dependence was observed.[12] This difference results from the much lower pK_a of surface sulfonic acid groups (ca. 2[38]) compared to the pK_a of ca. 5 for surface-bound ammonium groups.[38] In other words, unlike the a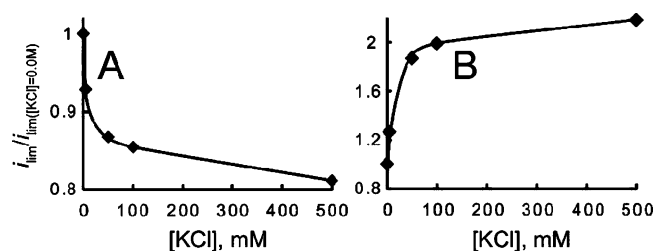mino groups that can become completely deprotonated and thus uncharged at or above neutral pH, a large portion of the sulfonic acid groups remains deprotonated and thus negatively charged in the entire pH range studied. The i_{lim} dependence then reflects only the additional deprotonation with pH increasing from 2 to 9. This suggests that at lower pH there is still present a portion of sulfonic acid groups that are protonated, which may be the result of repulsive interactions between the negatively charged $-SO_3^-$ groups on silica surface, leading to higher pK_a values for the remaining $-SO_3H$ groups at higher pH.[38]

Finally, to confirm that the above behavior resulted from the surface sulfonation, we investigated the pH dependence of $Ru(NH_3)_6^{3+}$ flux through the unmodified silica colloidal films and observed only very small changes in the limiting current at different pH (Figure SI2), which is similar to our earlier observations for $IrCl_6^{3-}$.[13]

Ionic Strength Effect on Diffusion through Sulfonated Colloidal Films. In order to demonstrate the electrostatic origin of the observed transport behavior in sulfonated colloidal films, we studied the diffusion of $Ru(NH_3)_6^{3+}$ and $IrCl_6^{3-}$ through the sulfonated films as a function of solution ionic strength, using KCl as the electrolyte at pH ~7 in water. Increasing the solution ionic strength reduces the diffusion rates for the positively charged species, $Ru(NH_3)_6^{3+}$ (Figure 6A), while the transport rate of the negatively charged species, $IrCl_6^{3-}$ (Figure 6B), increases with the increasing ionic strength. In the latter case, the half-wave potential, $E_{1/2}$, for oxidation of $IrCl_6^{3-}$ shifted to more positive potentials, a phenomenon explained earlier by the relative difference in the strength of ion pairing of $IrCl_6^{3-}$ and $IrCl_6^{2-}$ by the supporting electrolyte cation.[41]

To verify that the above effects are electrostatic in nature, we studied the diffusion of ferrocenedimethanol through the sulfonated films as a function of solution ionic strength, using KCl as the electrolyte at pH ~7 in water. We found no dependence of the molecular flux for this neutral molecule on the ionic strength of the contacting solution (Figure SI3).

These observations clearly demonstrate the electrostatic nature of the observed effects. Indeed, as electrolyte is added to the solution, it screens the charge of the surface sulfonic groups, allowing diffusion of the negatively charged species through the colloidal film and decreasing the attraction of the positively charged species. For the colloidal film comprising 180 nm silica spheres, the distance from the center of the pore to the nearest sphere surface is ca. 14 nm. For the transport measurements conducted at the electrolyte concentration of 0.1 M (Figure 4), the Debye screening length (κ^{-1}) is only ca. 1 nm. Assuming that the electric field extends ~$5\kappa^{-1}$ from the surface (corresponding to the distance where the potential decays to ~1% of the surface potential), the electric field extends over only a fraction (~5 nm or ~36%) of the effective pore width. We believe that this approximation underestimates the electrostatic effect because the noncylindrical pores in the colloidal film are effectively smaller

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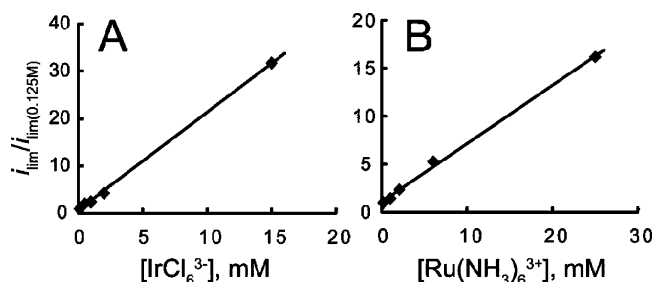(41) Watkins, J. J.; White, H. S. *Langmuir* **2004**, *20*, 5474.

Figure 7. Relative limiting current of sulfonated colloidal film electrodes as a function of concentration of (A) $IrCl_6^{3-}$ and (B) $Ru(NH_3)_6^{3+}$ in water.

than the distance between the center of the pore and sphere surface. We also speculate that the tortuous path that molecules take to diffuse through the colloidal film to reach the electrode and the high surface area of the colloidal crystal contribute to enhancing the electrostatic effects. In the light of these considerations, the observed ~19% blocking of the negatively charged species and the ~21% increase in the transport of the positively charged species are not surprising.

Transport Mechanism. Two different ion transport mechanisms may be proposed for the sulfonated colloidal films, i.e., a surface facilitated transport mechanism[42,43] for the positively charged species and diffusion through the free solution inside the nanopores for the negatively charged species. To gain an insight into the mechanism of the ion transport in the sulfonated colloidal films, we studied the dependence of the flux on the

concentration of the diffusing species in the 0.1−25 mM range. We found that the ionic flux increases linearly with the concentration for both redox active species (Figure 7). This suggests that transport in the sulfonated colloidal films, unlike colloidal membranes surface-modified with chiral receptor moieties,[14,15] is governed by the diffusion through solution inside the nanopores.

Conclusions

We demonstrated that the transport of positively charged species through sulfonated silica colloidal films is increased while the transport of the negatively charged species is blocked compared to the unmodified films. We showed that these effects are based on electrostatic attraction and repulsion modulated by pH and the Debye screening length of the electric field within the pores of the colloidal film. We also showed that the transport through these films occurs via diffusion through the free solution inside the nanopores. We are presently studying the proton transport though these nanoporous materials.

Supporting Information Available: Relative limiting current plots of a sulfonated colloidal film electrode as a function of pH for $Fc(MeOH)_2$, of an unmodified colloidal film electrode as a function of pH for $Ru(NH_3)_6^{3+}$, and of an unmodified colloidal film electrode as a function of [KCl] for $Fc(MeOH)_2$. This information is available free of charge via the Internet at http://pubs.acs.org.

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