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Oxygen Permeation in Perfluorinated Ionomers Based on the Reaction with the Methylviologen Cation Radical. An ESR and Optical Study

Biswanath Maiti† and Shulamith Schlick*

Department of Chemistry, University of Detroit Mercy, Detroit, Michigan 48219-3599

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The methylviologen dication MV^{2+} was reduced photochemically to its cation radical in water and in perfluorinated membranes, in the presence of $Ru(bpy)_3{}^{2+}$ as a sensitizer. The radical presence and concentration were determined from electron spin resonance (ESR) and optical spectra. The disappearance of the radical due to reaction with oxygen was used as a basis for the study of oxygen permeation through membranes swollen by water, methanol, and ethanol. The permeation coefficients for the swollen membranes are considerably larger than for polymers that do not contain ionic groups, indicating the importance of the solvent in the transport properties of the membranes. This result is an indirect proof for the connectivity of the ionic domains in the membranes. In membranes with long and short pendant chains the permeability coefficient is highest in membranes swollen by ethanol and lowest in membranes swollen by water. The enhanced permeability of oxygen in membranes swollen by the alcohols is related to the plasticizing effect of the solvent and is in agreement with recent ^{19}F NMR studies of dynamics in swollen membranes. The results also indicate that the major factors affecting oxygen transport are the presence and nature of the solvent and not the length of the pendant groups.

Introduction

The formation of the superoxide radical $O_2{}^-$ by electron transfer from Ti^{3+} to molecular oxygen has been studied by electron spin resonance (ESR) in perfluorinated ionomer membranes, in order to estimate the rate of oxygen diffusion.[1] The influence of Al^{3+}, Sc^{3+}, and Na^+, added as cocations in the process of membrane neutralization, on the rate of $O_2{}^-$ formation has also been investigated.[2] The effect of the cocation is specific: The rate of $O_2{}^-$ formation is significantly enhanced by the presence of Al^{3+}, an effect we explain by the reduced clustering of Ti^{3+} in the presence of Al^{3+}.

The method described above for the study of oxygen diffusion is applicable only to *dry* membranes, because the superoxide radical ion is not stable in protic media. In *very dry* membranes, however, oxygen diffusion is very slow and approaches the diffusion rate in Teflon.[3] The reduced diffusion rate was explained by the disappearance of the connecting channels between the ionic domains in the ionomer in the absence of solvent.[4,5] The applicability of this method for the study of oxygen penetration in swollen membranes is therefore limited.

In this study we will describe a method of measuring oxygen transport through swollen membranes, based on the photochemical generation of the methylviologen radical cation $MV^{\bullet+}$ from methylviologen MV^{2+} and its disappearance due to the reaction with oxygen. The radical is formed in the presence of $Ru(bpy)_3{}^{2+}$ (bpy is 2,2′-bipyridine) as a sensitizer and of triethanolamine (TEA) as a sacrificial donor D, as seen in reactions 1–4.[6-8]

$$Ru(bpy)_3{}^{2+} \xrightarrow{h\nu} Ru^*(bpy)_3{}^{2+} \qquad (1)$$

$$Ru^*(bpy)_3{}^{2+} + MV^{2+} \rightarrow Ru(bpy)_3{}^{3+} + MV^{\bullet+} \qquad (2)$$

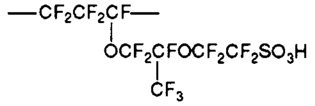
$$Ru(bpy)_3{}^{3+} + D \rightarrow Ru(bpy)_3{}^{2+} + D^+ \qquad (3)$$

$$2MV^{\bullet+} + O_2 + 2H_2O \rightarrow 2MV^{2+} + H_2O_2 + 2\,OH^- \qquad (4)$$

The methylviologen radical was generated in aqueous solutions and in the perfluorinated membranes, in a strictly oxygen-free atmosphere. In both cases, the decrease in the radical concentration due to reaction with oxygen was measured by ESR or by monitoring the absorbance at 604 nm, as a function of time.

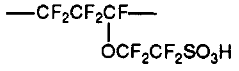
This study has been initiated with two main objectives. First, we were interested in comparing the effect of the solvent used to swell the membranes on oxygen transport. This interest has emerged from our previous studies, which indicated important solvent effects on the local environment of the cations and on the process of cation clustering.[9,10] Second, we wanted to compare the effect of the pendant chain length on oxygen permeability. This has been accomplished in this study by comparing the behavior of Nafion (long pendant chains) with that of the membranes made by Dow (short pendant chains).[11-13]

In this report we present a study of oxygen permeation in Nafion (I) and Dow (II) membranes neutralized by Na^+ and swollen by water, methanol, and ethanol.



$$\text{—}CF_2CF_2\underset{\underset{\underset{CF_3}{|}}{OCF_2CFOCF_2CF_2SO_3H}}{\overset{}{CF}}\text{—}$$

I, Nafion membrane, acid form



$$\text{—}CF_2CF_2\underset{OCF_2CF_2SO_3H}{CF}\text{—}$$

II, Dow membrane, acid form

Experimental Section

The Nafion 117 perfluorinated sulfonated membranes (I) with an equivalent weight of 1100 g of polymer/mol of SO_3H and a thickness of 0.178 mm were obtained from Du Pont. The dry Dow membranes (II) had a thickness of 0.09 mm and an equivalent

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† On leave from the Bhabha Atomic Research Centre, Bombay, India.

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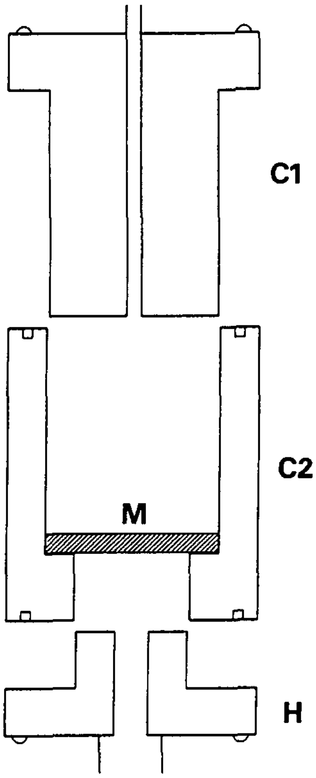

Figure 1. Cell for permeation measurements.

weight of about 800, estimated from wide-angle X-ray scattering and ^{19}F NMR.[14] All membranes were acidified and dried to constant weight in vacuo (10^{-4} Torr) as described previously[9,10,15] and soaked to constant weight with the corresponding solvent for at least 12 h in a glovebox. The thickness of the swollen membranes was measured with a micrometer to an accuracy of 0.005 mm. The thicknesses of Nafion swollen by water, methanol, and ethanol were 0.190, 0.240, and 0.260 mm, respectively. The corresponding values of the Dow membranes were 0.120, 0.180, and 0.200 mm.

Methylviologen MV^{2+} (*N,N'*-dimethyl-4,4'-bipyridinium as the dichloride) and $Ru(bpy)_3{}^{2+}$ from Sigma were used without further purification. Triethanolamine (TEA) and NaOH were Fisher reagent grade, and water was deionized and doubly distilled.

The generation of the methylviologen cation radical *in the membranes* was done by equilibrating the membranes successively with aqueous solutions of methylviologen dichloride and of the Ru(II) complex for 3 h and with 0.1 M TEA for 1 h. After adjustment of the pH to 11.5 with 0.2 M NaOH, the membranes were transferred to ESR sample tubes, degassed on the vacuum line by five freeze–thaw cycles, and irradiated for 15–20 min using glass and water filters. The radicals *in solution* were obtained by purging the aqueous mixture containing the reactants with nitrogen gas for 5 min, followed by UV irradiation. A typical solution contained 5×10^{-4} M MV^{2+}, 5×10^{-4} M $Ru(bpy)_3{}^{2+}$, 0.1 M TEA, and the amount of NaOH necessary to bring the pH to the range 11.0–11.5.

All irradiations were performed at ambient temperature using a low-pressure mercury source (Mineralight MODEL PCQX1) equipped with four no. 50053 tubes (Ultra-violet Products, San Gabriel, CA).

X-band ESR spectra were measured with a Bruker 200D SRC spectrometer operating at 9.7 GHz (empty cavity at ambient temperature) and 100-kHz magnetic field modulation, interfaced with a data acquisition system based on an IBM PC/XT and the software EPRDAS (Mega Systems Solutions, Rochester, NY). Samples were cooled using the Bruker flow system 4111VT. ESR spectra were plotted with the software SpectraCalc (Galactic Ind. Corp., Salem, NH).

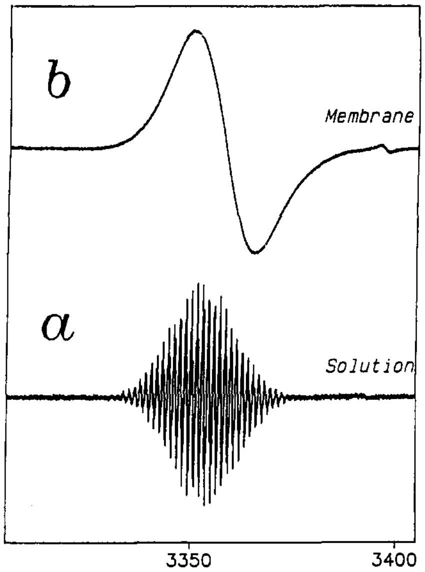

Figure 2. (a) X-band ESR spectrum at 300 K of the viologen cation radical in aqueous solutions. Microwave frequency is 9.423 57 GHz, microwave power is 2 mW, modulation amplitude is 0.4 G, and five scans were collected. (b) X-band ESR spectrum at 300 K of the viologen cation radical in Nafion containing 1% MV^{2+} and 1% Ru(II) complex. Microwave frequency is 9.421 85 GHz, microwave power is 2 mW, modulation amplitude is 2.5 G, and ten scans were collected.

Optical spectra were measured with the Hewlett-Packard 8452A diode array spectrophotometer.

Oxygen permeation through the membrane was measured using a cell made of Nylon (8 cm long, 3.8 cm o.d.), as shown in Figure 1. The gas inlet at the top can be kept open or tightly closed. The membrane M, supported by two Nylon gaskets, is placed between the two concentric cylinders C1 and C2. The cell can accommodate holder H for ESR or optical samples. In a typical experiment, the aqueous solution containing the reactants was thoroughly purged with nitrogen, the cell was assembled with the swollen membrane to be studied, and the sample tube containing the reactants was glued by epoxy to the bottom of the holder. All these operations were carried out in the glovebox under nitrogen. The inlet was then closed and the sample was irradiated with the UV lamp. The solution turned blue on irradiation, indicating the formation of the methylviologen cation radical. ESR spectra were recorded as a function of time after opening the inlet to oxygen. A quartz cell with a 1-cm path length was used for optical measurements. The absorbance at 604 nm was measured as a function of time after opening the inlet. The solution was stirred between optical measurements.

Results

ESR Measurements. The X-band ESR spectrum of the methylviologen radical cation at 300 K obtained by 15-min irradiation of an aqueous solution containing the reactants at pH = 11.5 is shown in Figure 2a. The rich spectrum is due to hyperfine interactions from two ^{14}N nuclei and six methyl protons with splittings of the order of 4 G and smaller splittings from the two sets of aromatic protons.[7]

The X-band ESR spectrum of the methylviologen radical cation in Nafion at 300 K is shown in Figure 2b. Similar spectra are obtained for the radical in the Dow membranes. The resolution is lost, for two possible reasons. The reduction of MV^{2+} to $MV^{\bullet+}$ is not complete, leading to line broadening arising from electron hopping between the radical and the dication. In addition, the water content in the membranes containing the radicals is reduced, compared to hydrated acid membranes, due to their full neutralization with Na^+, Ru^{2+}, and viologen cations, thus reducing the mobility of the radicals.[4,5] We

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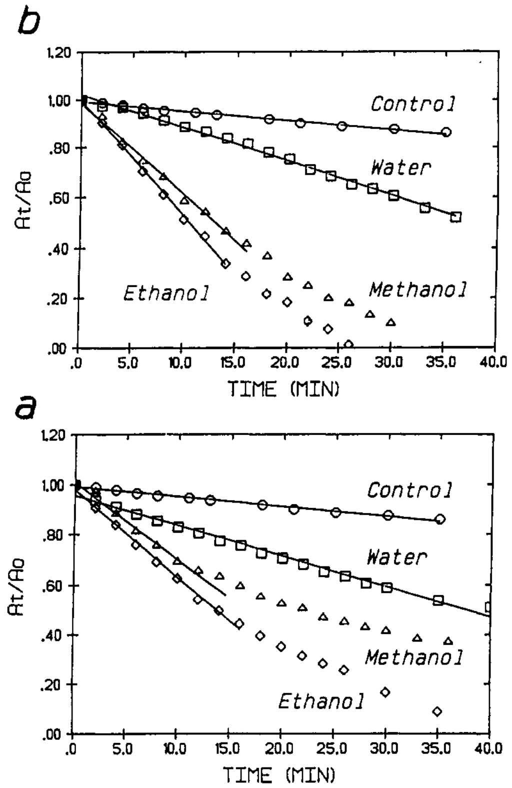

Figure 3. Normalized absorbance A_t/A_0 at 604 nm of the methylviologen cation radical as a function of time of exposure to atmospheric oxygen. (a) Nafion and (b) Dow membranes, swollen by water, methanol, and ethanol. The control set of data is also indicated.

note that a well-resolved ESR spectrum was obtained in Nafion, when the methylviologen radical cation was obtained by electrochemical reduction;[8] the high resolution in this case is probably due to the *complete* reduction of MV^{2+} and to *partial* neutralization of the sulfonic groups in Nafion.

The time required for complete oxidation of the cation radical at 3% neutralization of the membranes is of the order of hours; lower concentrations require shorter exposures to oxygen. This means that it is possible to perform this type of experiments at low oxygen pressures, typically 4 Torr. The major disadvantage of this method is the poor reproducibility of the measurements due to different sample packing, sample geometry, and amount of water in the membranes. Oxygen permeability in the cell shown in Figure 1 was measured by ESR; the limitation of this approach is that only relative permeability rates can be deduced, because the *absolute* radical concentration is very hard to measure and is subject to large experimental errors. This is due to the great sensitivity of the ESR signal intensity to the line widths, the sample size, and the exact position of the sample in the microwave cavity.

Optical Measurements. The absorption coefficient of the methylviologen radical in the membranes is not known; for this reason we chose to measure the permeability coefficient of oxygen through the membranes, by measuring the radical decay in solution, based on an extinction coefficient of 13 700 $dm^3\ mol^{-1}\ cm^{-1}$ for the methylviologen cation radical.[16] All optical results were obtained using the cell shown in Figure 1.

The results of the optical measurements, as the normalized absorbance A_t/A_0 at 604 nm vs time, are given in Figure 3 for the two types of membranes, swollen by water, methanol, and ethanol. The control plot, for the aqueous solution of the radical not exposed to oxygen, is also given and has been subtracted from the absorbances at the corresponding time of reaction. The experimental points represent data collected starting at a fixed time after the completion of the irradiation, normally 10 min.

Table I. Oxygen Permeability Coefficients from Optical Spectra

membrane	solvent	permeability coeff, barrer[a]
Nafion	water	80
Nafion	methanol	370
Nafion	ethanol	590
Dow	water	75
Dow	methanol	400
Dow	ethanol	580

[a] 1 barrer = 1×10^{-10} $cm^3(STP)\ cm/(cm^2\ s\ cmHg)$.

Discussion

The diffusion constants of gases through membranes are usually deduced by the steady-state method, from the time required to reach a constant gas diffusion current J (volume of gas at STP transported per unit area per unit time). This time is determined graphically by plotting the increase in the pressure of the diffused gas as a function of time.[17,18] If diffusion processes are very rapid, the time needed to reach the steady state is too short; in these cases the permeability coefficient P is measured, instead of the diffusion constant. In a permeation measurement the permeation coefficient P is obtained from the J values measured for a fixed pressure difference ΔP between the two sides of a membrane of thickness δ.[17-21] The permeability coefficient can then be calculated from eq 5.

$$P = J(\delta/\Delta P) \qquad (5)$$

The rate constant for the bimolecular oxidation reaction of the radical (reaction 4) is 7.7×10^8 $dm^3\ mol^{-1}\ s^{-1}$.[3] This rate is fast compared with the diffusion rate of oxygen through the membrane. Therefore the disappearance of the radicals is expected to be proportional to the amount of oxygen available. Under these conditions a plot of the absorbance as a function of time should be a straight line. The excellent straight lines obtained for the radical decay in both membranes swollen by water (Figure 3) suggest that this assumption is fulfilled.

For the membranes swollen by the alcohols, decay data follow a straight during the initial 15 min of reaction, but the decay is slower afterward. We propose that this effect is due to the loss of alcohol in the membrane and its replacement by water from the radical solution. In support of this suggestion is the fact that for longer reaction times the slopes for the membranes swollen by the alcohols are similar to those of the membranes swollen by water. Additional support for the suggestion that alcohols are replaced by water can be found in our previous studies of preferential solvation of Nafion membranes by various solvents, which indicate the dominant preference of the

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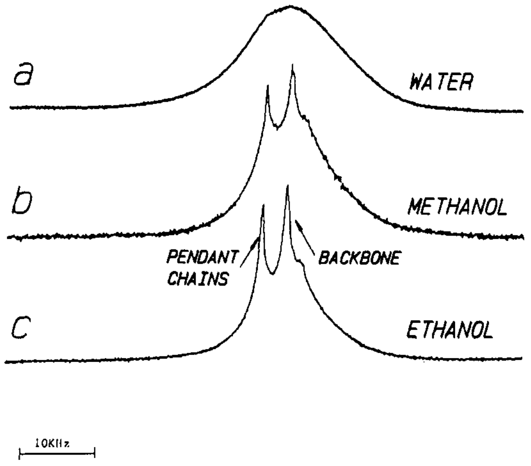

Figure 4. ^{19}F NMR spectra at 298 K and ν = 84.8 MHz of Nafion H membranes soaked by (a) water, (b) methanol, and (c) ethanol. Narrow signals from ^{19}F nuclei in the backbone and in the pendant chains are indicated (redrawn from ref 24).

membranes for water, as opposed to solvents of lower dielectric constants.[22] Therefore, for the calculation of the permeability coefficient P, we have taken into consideration only *initial* rates of decay for the membranes swollen by the alcohols.

The oxygen pressure $P(O_2)$ *above* the membranes is the oxygen pressure in air. The oxygen pressure *below* the membrane is small and probably negligible, because of the fast reaction with the viologen radical. With this assumption $\Delta P \approx P(O_2)$ in eq 5.

The data given in Figure 3 can be used to calculate the diffusion current J and the permeability coefficients P given in Table I for the two types of membranes swollen with the three solvents.

From the values given in Table I we can draw several conclusions.

First, all oxygen permeability coefficients for the swollen membranes are considerably larger than for a large number of polymers that do not contain ionic groups. For instance, the oxygen permeability coefficient is 0.110 barrer at 35 °C in amorphous poly(ethylene terephthalate) (PET) and 0.055 barrer in 42% crystalline PET.[20] The values in a series of silicone ring polymer are larger, in the range 28–35 barrer.[21] Comparison of these values indicate the importance of the solvent in the transport properties of the membranes and is an indirect proof for the connectivity of the ionic domains.

Second, in both types of membranes, the permeability coefficient is highest in membranes swollen by ethanol and lowest in membranes swollen by water. The sensitivity to the specific solvent is most likely due to the plasticizing effect of the solvent, and is in agreement with the conclusions based on our recent study of swollen membranes by ^{19}F NMR spectroscopy. In Figure 4 we present from that study ^{19}F NMR spectra of Nafion membranes swollen by water, methanol, and ethanol.[23] For water as solvent, only a broad signal is observed, with a width at half intensity of 15.9 kHz, typical of solid-state NMR spectra from rigid chains. In the case of the alcohols, however, narrow signals from ^{19}F nuclei inthe backbone and in the pendant chains are also detected in addition to the broad signal and represent nuclei with a high mobility and a correlation time of about 10^{-4} s. Spectra similar to those presented in Figure 4 have also been measured for the Dow membranes.[14] The narrow signals are a result of the penetration of the solvent into the organic phase. The signal from the mobile segments is stronger in ethanol compared with methanol and indicates more chains in contact with the solvent. This interpretation suggests that the major diffusion mechanism in membranes swollen by water is through the ionic domains. In the membranes swollen be alcohols, we propose *two* mechanisms for oxygen diffusion, through the ionic clusters and through the organic phase. The net result is an increased permeability of the membrane to oxygen, as detected experimentally.

Oxygen permeability in the membranes is expected to depend on the oxygen solubility in the swelling solvent. The solubilities are 0.0283, 0.2476, and 0.2417 g of oxygen/g of solvent for water, methanol, and ethanol respectively, at atmospheric pressure and 298 K.[24] These values could explain the enhanced permeability in the membranes swollen by the alcohols compared to water but *not* the observed difference between the effect of methanol and ethanol. The effect must be related to the polymer–solvent interactions and is reflected in the NMR spectra.

Third, data for the two types of membranes swollen by the same solvent are almost identical, suggesting that the major factor for oxygen transport is the presence of the solvent and not the structural differences.

A study of nitrogen permeation through Nafion neutralized by various cations has been published recently.[25] The permeability coefficient given for the Nafion membranes neutralized by Na^+ could be compared with our data; this is difficult however because the units of P in ref 25 are not clearly given.

The method we have developed for oxygen permeation is easy to apply and extremely sensitive to small quantities of oxygen. In addition, it could be applied to the specific detection of oxygen permeability out of a mixture of gases.

Conclusions

The methylviologen dication MV^{2+} can be reduced photochemically to its cation radical in aqueous solutions and in perfluorinated membranes, in the presence of $Ru(bpy)_3^{2+}$ as a sensitizer. The radical presence and concentration can be determined from ESR and optical spectra. The disappearance of the radical due to reaction with oxygen was used as a basis for the study of oxygen permeation through membranes swollen by water, methanol and ethanol.

The permeation coefficients for the swollen membranes are considerably larger than for a large number of polymers that do not contain ionic groups, indicating the importance of the solvent in the transport properties of the membranes, and is an indirect proof for the connectivity of the ionic domains in the membranes. In membranes with long and short pendant chains the permeability coefficient is highest in membranes swollen by ethanol and lowest in membranes swollen by water. The sensitivity to the specific solvent is most likely due to the plasticizing effect of the solvent, in agreement with the recent ^{19}F NMR studies of dynamics in swollen membranes. The results also indicate that the major factor affecting oxygen transport is the presence of the solvent and not the size of the pendant chain.

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Registry No. MV^{2+}, 1910-42-5; $Ru(bpy)_3^{2+}$, 15158-62-0; O_2, 7782-44-7; H_2O, 7732-18-5; MeOH, 67-56-1; EtOH, 64-17-5; Nafion 117, 66796-30-3.

Preparation, Characterization, and Ionic Conductivity of Novel Crystalline, Microporous Germanates, $M_3HGe_7O_{16}\cdot xH_2O$, M = NH_4^+, Li^+, K^+, Rb^+, Cs^+; x = 4–6. 2

Shouhua Feng and Martha Greenblatt*

Department of Chemistry, Rutgers, The State University of New Jersey,
Piscataway, New Jersey 08855-0939

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A series of crystalline, microporous germanates, $M_3HGe_7O_{16}\cdot xH_2O$, M = NH_4^+, Li^+, $x = 6$; M = K^+, Rb^+, Cs^+, $x = 4$, were synthesized hydrothermally and characterized by powder X-ray diffraction, differential thermal analysis, and thermogravimetric analysis. Ionic conductivity in both hydrated and dehydrated samples was investigated by ac impedance in the temperature range 25–550 °C. The protonic conductivity is highest in $(NH_4)_3HGe_7O_{16}\cdot 6H_2O$, 3.1×10^{-4} $(\Omega\ cm)^{-1}$ at 144 °C. The best ionic conductivity was found in $Cs_3HGe_7O_{16}$, 2.0×10^{-3} $(\Omega\ cm)^{-1}$ at 400 °C. The ionic conductivity of dehydrated $M_3HGe_7O_{16}$ increases and the activation energy decreases with increasing cation radius from room temperature to 500 °C. This behavior is consistent with a reduced Coulombic attraction between the mixed tetrahedral–octahedral (GeO_4–GeO_6) anion framework structure of the germanates and the cations located in their channels, compared with that in other zeolite-type compounds.

1. Introduction

Crystalline microporous materials are widely used in the fields of catalysis, ion exchange, and adsorption.[1-3] There have been many attempts to develop and improve electrical conductivity in the crystalline microporous materials, which contain open channels on the molecular scale and exchangeable cations; the channels serve as conducting paths for the mobile ions. Ionic conductivity studies in a number of aluminosilicate zeolites have been made, with special focus on the ion-exchange properties of zeolite samples and on the effect of different channel dimensions (i.e., aperture size) on the ionic conductivity.[4-10] However, the ionic conductivity in these materials is low compared to known fast ionic conductors. The reasons for the low conductivity in zeolitic materials are 2-fold: (1) the negatively charged framework structure of traditional zeolites has very strong attraction for cations, which hinders ion migration;[11] (2) the size of channels or cages in some of the zeolites is so large that the mobile ions are trapped on the walls of the channels or cages. Thus decreasing the electrostatic interaction between the anion framework structure and the cations and matching the ion-channel size are important factors in improving ionic conductivity of zeolitic materials. To investigate these effects, we have chosen a novel crystalline microporous sodium hydrogen germanate, $Na_3HGe_7O_{16}\cdot xH_2O$, with a mixed, tetrahedral–octahedral framework structure closely related to zeolitic materials.[12-20] Previous studies on $Na_3HGe_7O_{16}\cdot xH_2O$ showed protonic conductivity $\sim 10^{-4}$ $(\Omega\ cm)^{-1}$ at 50 °C and sodium ionic conductivity $\sim 10^{-3}$ $(\Omega\ cm)^{-1}$ at 500 °C on dehydrated samples.[21] We have continued to investigate ionic conductivity in this structure with other ions, in order to understand the mechanism of ionic conduction and to search for fast ionic conductors in zeolite-like materials. The crystalline microporous germanates, $M_3HGe_7O_{16}\cdot 4$–

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