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Mobility of Li^+, Na^+, and Cs^+ cations in Nafion membrane, as studied by NMR techniques

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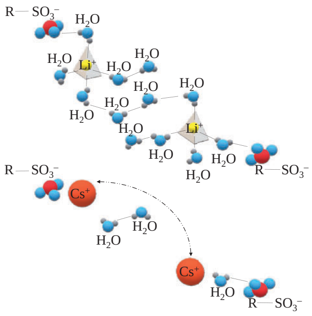
The local mobility and diffusion of Li^+, Na^+, and Cs^+ cations in Nafion 117 membrane were explored by ^{7}Li, ^{23}Na, and ^{133}Cs spin relaxation and pulsed field gradient NMR techniques. It was shown that the macroscopic mass transfer of cations is controlled by ion motion near sulfonate groups. Lithium and sodium cations, whose hydrated energy is higher than the water hydrogen bond energy, are moving together with water molecules, but cesium cations possessing a low hydrated energy are jumping directly between the neighboring sulfonate groups.



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Ionic transport in cation-exchange membranes is controlled by the nanostructure of ionogenic channels and particularities of cation hydration.[1,2] To reveal the transport mechanism, the mobility of cations in different spatial scales should be studied. NMR spectroscopy is widely used for studying the structure and dynamics of complicated molecular systems.[3–5] Nuclear spin relaxation and pulsed field gradient (PFG) NMR are very attractive techniques for describing molecular and ionic mobility in polymeric electrolytes. Interesting and fundamental results were obtained for the transport of water molecules and alkaline cations in sulfonated cation-exchange membranes. Perfluorinated Nafion (including modified Nafion) and MF-4SC membranes are of special interest.[6–21] Diffusion of water molecules and Li^+ cations at different water contents was investigated by PFG NMR. A correlation between cation hydration numbers and self-diffusion was revealed.[6,7] Spin relaxation of the ^{1}H (water molecule) and ^{7}Li (lithium cation) nuclei gave an opportunity to calculate the correlation times of water and Li^+ in the Li^+ ionic form of the MF-4SC membrane. It was concluded that the local mobility of molecules and cations near sulfonate groups governs its macroscopic transport.[6,12,17] The mobility of other alkaline cations was almost not studied except for publications devoted to the relaxation and diffusion of ^{23}Na in polystyrene sulfonate systems[22–25] and $^7Li^+$, $^{23}Na^+$, and $^{133}Cs^+$ cations in membranes based on polyethylene and grafted sulfonated polystyrene[26] examined by a combined application of spin relaxation and PFG NMR techniques. Local mobility studies are especially important for alkali metal cations with different hydration capacities, such as Li^+, Na^+, and Cs^+, since they clarify the microscopic mechanism of ionic membrane selectivity. A comparison of the local mobility characterized by correlation times and the macroscopic mobility characterized by diffusion coefficients allowed us to understand the morphology of membrane transport paths.

Mobility and self-diffusion peculiarities of Li^+, Na^+, and Cs^+ cations in a Nafion 117 membrane were revealed by ^{7}Li, ^{23}Na, and ^{133}Cs spin relaxation and PFG NMR techniques.

Figure 1 shows the temperature dependences of the diffusion coefficients of (*1*, *1'*, *1''*) Li^+, (*2*) Na^+, and (*3*) Cs^+ in the Li^+, Na^+, and Cs^+ ionic forms of Nafion 117.

The temperature dependences are approximated by the Arrhenius equation

$$D = D_0 \exp(-E_a/RT), \qquad (1)$$

where D_0 is the temperature independent preexponential factor, R is gas constant, T is absolute temperature, and E_a is diffusion activation energy.

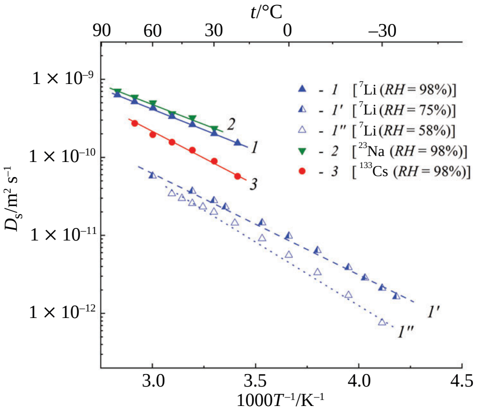

Figure 1 Temperature dependences of the diffusion coefficients of (*1*, *1'*, *1''*) Li^+, (*2*) Na^+, and (*3*) Cs^+ in the corresponding ionic forms of Nafion 117 for samples contacting water (*1*, *2*, *3*) (reprinted with permission from ref. 7). Curves *1'* and *1''* show the temperature dependences of Li^+ diffusion coefficient at RH = 75 and 58%, respectively.

The activation energies of Li^+ cations are 20.5 kJ mol^{-1} for a sample contacting with water (curve *1*), 25.3 kJ mol^{-1} for a sample at *RH* = 75% (curve *1′*), and 30.4 kJ mol^{-1} for a sample at *RH* = 58% (curve *1″*). The activation energies of sodium and cesium cations are 19.3 (curve *2*) and 24.8 kJ mol^{-1} (curve *3*) for samples equilibrated with water.

Figure 2 shows the temperature dependences of the spin–lattice and spin–spin relaxation times of ^7Li, ^{23}Na, and ^{133}Cs.

At *RH* = 75%, the functions $T_1(T)$ and $T_2(T)$ of ^7Li and ^{23}Na decreased with decreasing temperature [Figure 2(*a*), curves *1* and *2*, *2′*] due to the fast narrowing conditions [$(\omega\tau)^2 << 1$], but T_1 for ^{133}Cs increased with decreasing temperature [$1 < (\omega\tau)^2$] [Figure 2(*a*), curve *3*]. The ^{133}Cs function $T_1(T)$ showed a minimum in samples equilibrated with water. Unfortunately, it was impossible to measure T_1 of ^7Li and ^{23}Na at temperatures below –40 °C in order to observe a spin relaxation minimum of these nuclei [Figure 2(*b*)]. The activation energies of ^7Li spin relaxation are about 20 kJ mol^{-1}, which is close to the activation energy of Li^+ diffusion. The activation energies of ^{23}Na spin relaxation and diffusion are also close to each other (20 kJ mol^{-1}) in the samples equilibrated with water.[7] As shown in Figure 2(*b*), the temperature dependences of ^7Li and ^{23}Na spin–lattice relaxation have a plateau. The temperature of the ^7Li spin-relaxation time minimum can roughly be estimated at about 233 K from the approximation of $T_1(T)$ by a Gaussian function. According to ref. 24, T_1 $(\omega\tau_{av})^2 \approx 1$ and $\tau_{av} = 10^{-9}$ s at the minimum. At this temperature, the Li^+ diffusion coefficient D is 4×10^{-12} m^2 s^{-1} (Figure 1). From the Einstein equation, the self-diffusion coefficient can be calculated as

$$D = l^2/6\tau_{av}, \tag{2}$$

where l is the average jumping distance.

Thus, the value of l is $(6D\ \tau_{av})^{1/2}$. For the Li^+ cation, l is 0.15 nm, which is close to the water hydrogen bond length. It can be supposed that the translation displacement of Li^+ is controlled by a rearrangement of hydrogen bonds of hydrated water molecules, which explains a symbatic behavior of water and lithium cation diffusion.[6,7] The temperature dependence $T_1(T)$ for ^{133}Cs shows a minimum at 20 °C [Figure 2(*b*), curve *3*]. In spite of the fact that the ^{133}Cs spin is 7/2, we can crudely estimate the correlation time at this temperature from the relationship $(\omega\tau_{av})^2 \approx 1$, and τ_{av} is 3×10^{-9} s. The diffusion coefficient of cesium cations at this temperature is 3×10^{-11} m^2 s^{-1} (Figure 1), and l is about 0.7 nm. This value is equal to an average distance between the neighboring sulfonate groups.[6] Therefore, it can be assumed that τ_{av} estimated from ^{133}Cs spin lattice relaxation is the time of cesium cation jumping between SO_3^- groups. It looks very likely because the electric field gradient *eq* is dramatically changed when the cations approach or depart the sulfonate group.

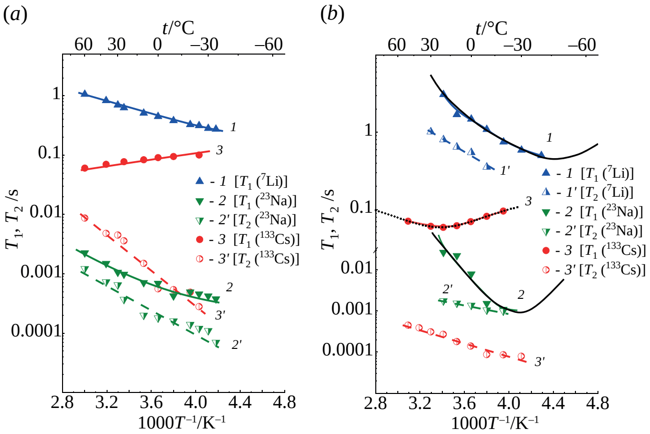

Figure 2 Temperature dependences of the spin–lattice and spin–spin relaxation times (*1*, *2*, *3*) T_1 and (*1′*, *2′*, *3′*) T_2, respectively, of (*1*, *1′*) ^7Li, (*2*, *2′*) ^{23}Na, and (*3*, *3′*) ^{133}Cs in the Li^+, Na^+, and Cs^+ ionic forms of Nafion 117 membrane. (*a*) Samples equilibrated with water vapor at *RH* = 75%; (*b*) samples in contact with water. Dotted lines show Gaussian function approximations.

Thus, spin relaxation and pulsed field gradient NMR techniques were applied to ^7Li, ^{23}Na, and ^{133}Cs in order to reveal cation transfer particularities in different spatial scales in the Nafion 117 membrane. An analysis of the temperature dependences of spin–lattice and spin–spin relaxation times gave an opportunity to estimate correlation times of local motion of Li^+, Na^+, and Cs^+ cations. The diffusion coefficients calculated from the Einstein equation were compared with the macroscopic diffusion coefficients measured by pulsed field gradient NMR. It was concluded that the macroscopic transfer is controlled by the ion motion near sulfonate groups. The lithium cation translation displacement is controlled by a rearrangement of hydrogen bonds in hydrated water molecules, which explains a symbatic behavior of water and lithium cation self-diffusion. It can be assumed that Li^+ and Na^+ cesium cation jumping occurs directly between the SO_3^- groups.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2023.02.021.

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