Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 215–217

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

Nikita A. Slesarenko, Alexander V. Chernyak, Irina A. Avilova, Victor P. Tarasov and Vitaly I. Volkov

Materials and methods

Extruded N117 (thickness 183 μm, equivalent weight (*EW*)=1100, Dupont, Ion Power Inc.) membranes were used for the experimental characterization of Nafion in salt (Li^+, Na^+, Cs^+) ionic form.

Diffusion coefficients were measured by pulsed field gradient technique of ^{7}Li, ^{23}Na, ^{133}Cs nuclei at frequencies 155.51, 105.84, 52.48 MHz, respectively, on Bruker AVANCE-III-400 NMR spectrometer, equipped with the diff-60 gradient unit. The pulsed field gradient stimulated echo sequence was applied[S1,S2] .

The evolution of spin echo signal is described by the following equation:

$$A(g) = A(0)\exp(-\gamma^2 g^2 \delta^2 t_d D_s), \quad (1)$$

where γ is nuclear gyromagnetic ratio, g is gradient pulse amplitude, δ is gradient pulse duration, $t_d = \Delta - \delta/3$ is the diffusion time, Δ is an interval between gradient pulses and D_s is the diffusion coefficient. The gradient strength was varied linearly in 32 steps within a range from 0.1 to 27 T/m value. The integrated intensities of spectrum lines were used to obtain the dependence of echo signal attenuation on g^2 (diffusion decay).

Experimental diffusion decays are well approximated by equation 1 in 2-3 orders of magnitudes, diffusion coefficient measurement error was less than 10%.

Spin-lattice T_1 and spin-spin T_2 nuclear relaxation times were measured using 180°-τ-90° and Carr-Purcell-Meiboom-Gill (90°-τ-n180°) pulsed sequences, correspondingly. Longitudinal magnetization M_z recovery and transverse magnetization $M_{x.y}$ decay were approximated by exponential dependences for ^{7}Li, ^{23}Na, ^{133}Cs nuclei.

NMR spectra of ^{7}Li, ^{23}Na and ^{133}Cs nuclei belong to Li^+, Na^+ and Cs^+ cations are singlet lines, which width is rather narrow even at temperature below 0°C that indicates the high cation mobility at low temperature.

The nuclear spins of ^{7}Li, ^{23}Na are 3/2, but ^{133}Cs nuclear spin is 7/2. For these nuclei the main relaxation mechanism is quadrupole relaxation. For nuclear spin is 3/2:

$$\frac{(M_z - M_0)}{M(cos\theta - 1)} = \frac{1}{5}\exp(-2J_1 t) + \frac{4}{5}\exp(-2J_2 t), \quad (2)$$

$$\frac{M_{x,y}}{M_0} sin\theta = \frac{3}{5}[-(J_0 + J_1)t] + \frac{2}{5}[-(J_1 + J_2)t], \quad (3)$$

where ω – NMR frequency; Θ – a rotation angle of equilibrium magnetization M_0 during radio frequency pulse; $J(\lambda\omega)$ – spectral densities on the frequencies $\lambda\omega$ (λ=0, 1, 2).

$$J_\lambda = 0.1 \cdot \pi^2 \cdot \chi^2 \cdot J(\lambda\omega), \quad (4)$$

$$\chi = eQ \cdot \frac{eq}{h}, \quad (5)$$

where τ – correlation time; E_a – activation energy.

Equations (2), (3) are exponential at short correlation time if $(\omega\tau)^2 << 1$. Magnetization kinetic curves are exponential at high temperature. With temperature decreasing magnetization $1 \leq (\omega\tau)^2$ and kinetic curves should be two exponential shape, but it may be not success to observe two exponential curves experimentally especially for longitude magnetization recovery.

References

S1. V. I. Volkov, A. V. Chernyak, N. A. Slesarenko and I. A. Avilova, *Int. J. Mol. Sci.*, 2022, **23**, 5011.

S2. V. I. Volkov, A. V. Chernyak, O. I. Gnezdilov and V. D. Skirda, *Solid State Ion.*, 2021, **364**, 115627.

S3. I. A. Nesterov, V. I. Volkov, K. K. Pukhov and S. F. Timashev, *Russ. J. Chem. Phys.*, 1990, **91**, 155 (in Russian).

S4. B. Halle, D. Bratko and L. Puculell, *Ber. Bunsenges. Phys. Chem.*, 1985, **89**, 1254.

S5. B. Halle, H. Wennerstror and L. Piculell, *J. Phys. Chem.* 1984, **88**, 2482.

S6. R. H. Tromp, J. R. C. van der Maarel, J. de Bleijser and J.C. Leyte, *Biophys. Chem.*, 1991, **41**, 81.

S7. U. Böhme, B. Hänel and U. Scheler, in *Prog. Colloid Polym. Sci.*, eds. V. Starov, K. Prochazka, Springer, Heidelberg, 2010, vol. 138, pp. 45-49.

S8. V. I. Volkov, N. A. Slesarenko, A. V. Chernyak, V. A. Zabrodin, D. V. Golubenko, V. A Tverskoy and A. B. Yaroslavtsev, *Membr. Membr. Technol.*, 2022, **4**, 189 (*Membr. Membr. Tekhnol.*, 2022, **3**, 214).