

Direct in Situ Observation of Dynamic Transport for Electrolyte Components by NMR Combined with Electrochemical Measurements

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Electrochemical studies provide broad, but not cation- or anion-specific information on the migration of charged ions. However, individual ion diffusion (as a weighted average of charged and neutral ions) can be measured using pulsed-gradient spin-echo (PGSE) NMR. In this paper, the lithium transport in an electrolyte including a lithium salt was measured using electrophoretic NMR (ENMR) with non-blocking electrodes. A propylene carbonate (PC) solution doped with $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (LiTFSI) was inserted in a homemade NMR cell equipped with Li/Li electrodes. The drift migrations of lithium cation (^7Li), anion (^{19}F), and solvent (^1H) were measured independently under potentials of up to 3.0 V. Greatly enhanced dynamic lithium transport was observed for the first time in the bulk electrolyte under an electric field closely related to real conditions in a rechargeable lithium battery.

The electrolytes used in electrochemical devices such as batteries, capacitors, and actuators can receive external stimulation through the electrodes and complete the operations by charge/discharge processes, electrochemical polarization, mechanical movements, and so on. The observation of the responses under the external field is desirable to understand the actual ion behaviors in the electrolytes.¹ In particular, the ion drift migration under a static electric field is one of the most important subjects in electrochemistry, and voltage-current behaviors detected on electrodes have been well studied; however, the ion drift migrations in the bulk electrolytes are not yet well understood. The PGSE NMR method² can provide individual ion self-diffusion coefficients in electrolytes. In addition, using ENMR^{3–5} the in situ observation of ion drift migration is possible under an electric field using an NMR cell equipped with the electrodes. Also ENMR measurements were tried for the lithium polymer gel electrolytes using blocking electrodes.^{6,7} However, previous measurements were made under the assumption that the ion drift migration starts just after the voltage application. Actually, a delay time is necessary for the ion drift migration as long as an NMR cell with a reasonable sample volume is used. In this paper, the target is electrolytes for rechargeable lithium batteries and both electrodes are made of lithium metal which can react with the lithium ions in the electrolyte.

Solution electrolytes⁸ used in rechargeable lithium batteries consist of organic solvents and lithium salts such as LiPF_6 , LiBF_4 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (LiTFSI), and others. The lithium cationic transference number is assumed to relate with the performance

of lithium batteries, but its electrochemical evaluation is limited because of the difficulties involved in separating the motion of the lithium cations from the counter anions. On the other hand, the self-diffusion coefficients of the lithium cations, anions, and solvents can be individually measured using PGSE-NMR.^{9–13} However, PGSE NMR does not discriminate between charged ions and neutral ion pairs. Experimentally, we have confirmed that the PGSE-NMR and electrochemical measurements are closely related at infinitesimal concentration in the lithium solution electrolytes.⁸ The lithium cationic transference number $N_{\text{transference}}(\text{NMR})$ can be simply calculated from the self-diffusion coefficients of the lithium (D_+) and the anion (D_-) as $D_+/(D_+ + D_-)$. Usually, they are less than 0.5 in the solution electrolytes^{9–12} and smaller in gel-polymer electrolytes (about 0.2),^{13,14} and much smaller in the genuine-polymer electrolytes^{15–19} due to the slow matrix mobility affecting the lithium ion diffusion.^{20–22} The electrochemical estimation of the lithium transference numbers from the direct current polarization is similar but not exactly the same as the NMR estimation. The dominant migration of the lithium ions is believed to be essential to design advanced rechargeable lithium batteries.

We have been studying the self-diffusion coefficients of the individual components of propylene carbonate (PC) solution electrolytes doped with LiTFSI.⁸ Without the electric field, the self-diffusion coefficient D is measured by using the modified Hahn pulse sequence shown in Figure 1b. Usually, by changing the strength (g) or the width (δ) of the pulsed field gradient (PFG), the echo-signal attenuation (E) is analyzed using the Stejskal equation,²³

$$E = \exp\left(-\gamma^2 \delta^2 g^2 D \left(\Delta - \frac{\delta}{3}\right)\right) \quad (1)$$

where γ is the gyromagnetic ratio. For the solution electrolytes,

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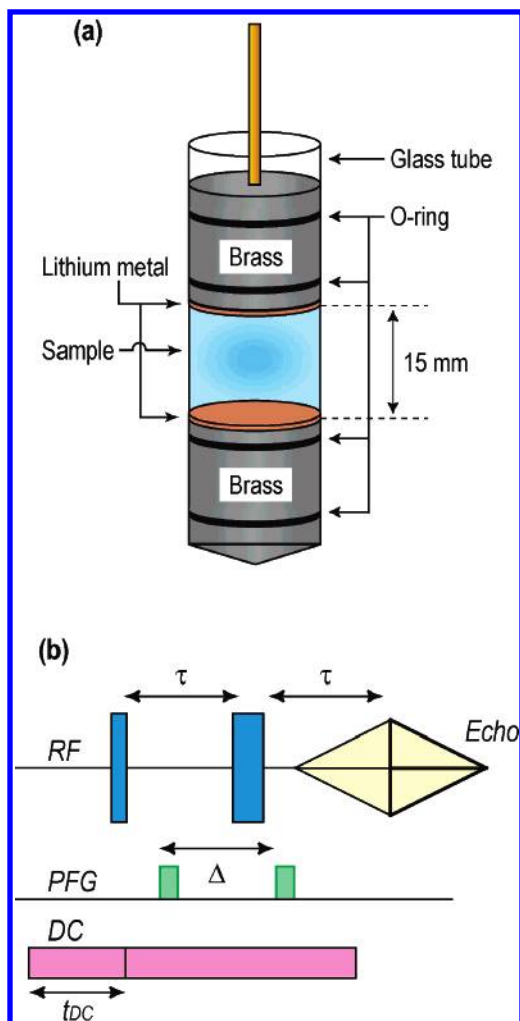


Figure 1. (a) Cell with Li–Li electrodes for the NMR and chronoamperometry measurements. The diameter of the glass tube was 10 mm, containing 0.3-mm thick lithium metal electrodes. The other metal parts were made of brass and connected to the glass tube by four O-rings. The height of the sample window was 15 mm to guarantee the constancy of the PFG in the vertical direction parallel to the external static magnetic field of 6.35 T. (b) The pulse sequence used for the ENMR measurements including the delay time t_{DC} . Without the imposition of the electric field, the pulse sequence is a standard Hahn echo-based PGSE-NMR sequence.²³

the plots of E are always single exponential. Under the electric field including the drift velocity v for the migrating nuclei the echo signal attenuation is described by⁴

$$E = \frac{S_v}{S_0} \cos(\gamma g v \Delta) \exp\left(-\gamma^2 \delta^2 g^2 D \left(\Delta - \frac{\delta}{3}\right)\right) \quad (2)$$

where S_v and S_0 are the echo signals in the presence and absence of the electric field, respectively.

In the PC–LiTFSI solution electrolytes in the absence of the electric field, the solvent (i.e., PC) diffuses the fastest, followed by anion TFSI and then the lithium ions. This trend always holds in lithium battery solution electrolytes, independent of the salt concentration.⁹ The lithium ions solvated by PC molecules have effectively larger radii, which result in the slowest self-diffusion.

The ENMR method, which is a PGSE measurement performed in the presence of an electric field, has been used for many applications.^{3–5} However, since the previous studies focused on the NMR aspects and were performed under the assumption that ion drift migration occurs instantaneously with

the imposition of the electric field, the pulse sequences did not include any delay time. However, chronoamperometry measurements indicate that an interval is required for the acceleration of the ion drift migration.

In the present study, a homemade NMR cell equipped with the Li/Li electrodes was used (Figure 1a). A PC solution containing LiTFSI (0.5 M) was adopted as a model of the solution electrolytes for rechargeable lithium batteries. The electrolyte was inserted into the cell in a dry-argon-filled glovebox ($[O_2] < 0.4$ ppm, $[H_2O] < 0.1$ ppm), Miwa MFG Co., Ltd. The cell configuration is Li/electrolyte/Li for a non-blocking cell. Under a static electric field, the drift migration of the lithium cation (^7Li), anion (TFSI) (^{19}F), and solvent (PC) (^1H) was observed using a JEOL probe where the static electric field and the PFG were applied in the same direction as the static magnetic field (6.35 T). The $\pi/2$ pulse widths were about 45 μs . The ^7Li , ^{19}F , and ^1H NMR resonance frequencies were 105, 254, and 270 MHz, respectively. The NMR measurements were conducted at 30 $^\circ\text{C}$. The maximum PFG strength was 0.94 T/m, and the interval Δ was fixed to 30 ms. Since the drift migration was sensitive to the surface conditions of the lithium electrodes, special care was taken in maintaining a clean surface on the electrodes.

Initially, the self-diffusion coefficients of the Li, TFSI, and PC were measured for the 0.5 M LiTFSI PC solution confined in the cell in Figure 1a without electric field. The values were 2.7, 3.2, and $4.4 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ for Li, TFSI, and PC, respectively. The maximum voltage used in the NMR experiments was 3 V, since it is well-known that the present sample is electrochemically unstable above 3.5 V. To include the delay time t_{DC} for the drift migration after the application of the electric field, the pulse sequence shown in Figure 1b was used for the ENMR measurements. When the static electric field up to 3 V was applied at $t_{DC} = 0$, the attenuation of the echo signals of the ^7Li and ^{19}F resonances was changed a little without phase distortion. The solvent attenuation was almost unchanged even as t_{DC} was increased. This suggests negligible convection effects in the ENMR experiments.⁵ In the present experimental setup, no phase distortion of the echo signals was observed throughout the experiments. The attenuation of the echo signals of the lithium cation and TFSI anion was enhanced by the application of the electric field when the t_{DC} became longer and the applied voltage became larger. As the electric field effect increased, the PFG strength was necessarily reduced to accurately measure the echo attenuations. By using the D values without electric field, the drift velocity v was calculated by analyzing the attenuation of the echo signals using eq 2. An example of the attenuation plots for the lithium ion is given in Figure S2 in the Supporting Information. The applied voltage was monitored by a Keyence NR-500/NR-HA08 digital data recorder.

In the cell with lithium electrodes, since the dissolution and the deposition of the lithium ions on the lithium metal surface can occur under the electric field, the one-directional migration of the lithium ions from positive to negative electrodes can be assumed to produce a continuous electric current, while the actual migration behaviors of the lithium ions, anions, and solvents in the bulk have not yet been observed. At first we measured the current density at 30 $^\circ\text{C}$ by electrochemical chronoamperometry using a computer-controlled potentiostat/galvanostat (PAR VMP2/Z), which measures the electric current detected by the electrodes. Thus, this measurement provides information on all of the charged ions near the electrodes. The chronoamperometric responses against the applied voltage are shown in Figure 2 for (a) the initial stage and (b) the long-term

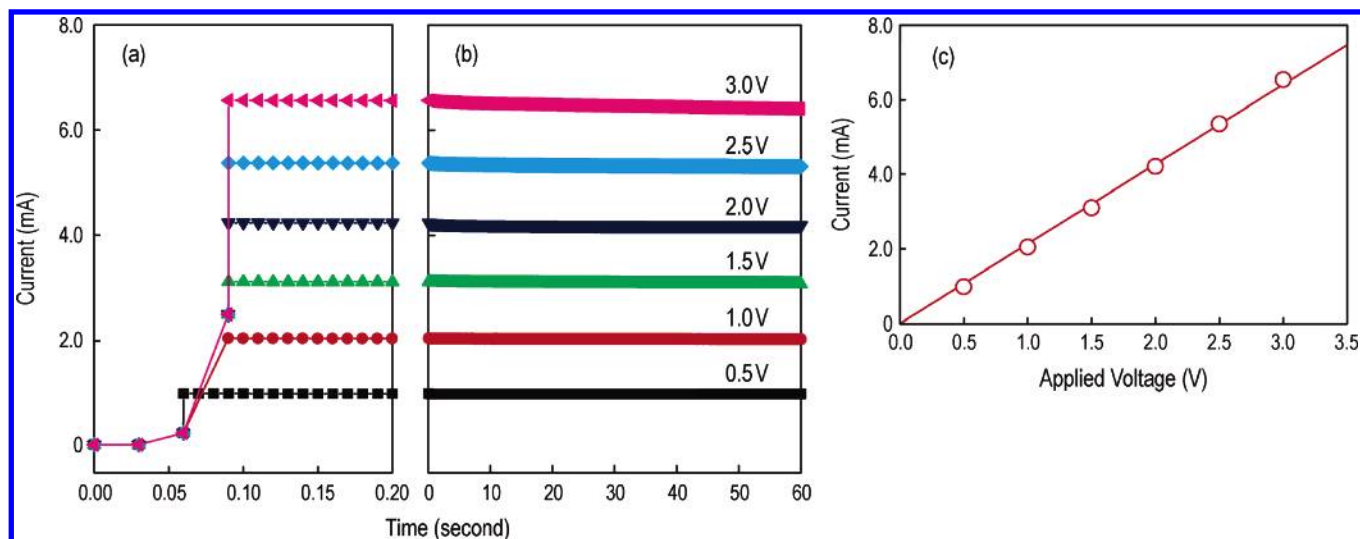


Figure 2. Current responses of the chronoamperometry measurements for the (a) initial and (b) steady states. The current responses were almost identical in the standard cells containing the lithium electrolytes used for testing. Panel (c) shows the relationships between the applied voltage and the steady current density for the NMR cell with Li/Li electrodes. The steady current density changed linearly with the applied voltage. Therefore, the total cell resistance was not changed during the electrochemical measurements, and the side reactions such as the formation of SEI layer on the lithium surface or decomposition of PC/LiTFSI electrolyte solution can be neglected in the present experiments. In addition to the preliminary measurements, since the electrochemical measurements in (c) were made after the NMR measurements, the cell was stable during the entire experimental period. The steady current density enabled the evaluation of total cell resistance from Ohm's law ($V = IR$). The obtained resistance value was $468 \, \Omega$.

responses from 0.5 to 3.0 V. A linear response of the current versus the electric field following Ohm's law was obtained in the steady state from 0.5 to 3.0 V as shown in Figure 2c. A delay time required to reach the steady current was necessary and shorter than 0.1 s depending on the applied voltage to the electrodes.

The ENMR measurements for the Li cation (^7Li) and the anion (^{19}F) were made by applying a 2.0 V electric field and changing the delay time t_{DC} . The PGSE attenuations were almost single exponentials. By using eq 2, the ion drift velocity v was calculated from the PGSE attenuation and the delay time dependencies of the lithium and anion (TFSI) drift velocities are shown in Figure 3a. The calculated drift velocity at $t_{\text{DC}} = 0$ was small for both the lithium cation and the TFSI anion. As t_{DC} became longer, the lithium drift velocity increased greatly until 0.6 s and decreased a little, while the increase of the anion drift velocity was much smaller. Without the electric field, the lithium transference number was 0.45 in the present cell. As the t_{DC} increased, the lithium drift migration was more enhanced than the anion drift migration. The ion drift velocity induced by the potential difference between the electrodes is an averaged value over the whole electrolyte solution. The delay time required to reach the maximum value for the lithium was about 0.6 s, while the anion velocity reached an equilibrium state with a delay longer than 0.6 s, and both are longer than the time delay measured by chronoamperometry. The ion drift migration in the bulk electrolyte solution occurs more slowly than the electric current near the electrodes. Under the electric field of the Li/Li electrodes, it was demonstrated that the electric current is produced predominantly by the lithium ion drift migration.

The measurements were made for the lithium ion, anion and solvent by fixing t_{DC} at 0.4 s. Since no phase distortion of the echo signals was observed, the apparent diffusion coefficients were calculated using eq 1 and are plotted in Figure S3 in the Supporting Information. The ion drift velocities calculated using eq 2 are plotted for the lithium ion and TFSI versus the strength of the applied voltage in Figure 3b. The apparent diffusion coefficients of the solvent (i.e., PC) were unchanged, as shown

in Figure S3, and the anion diffusion plot under 1.0 V overlapped with that obtained at 0 V. The self-diffusion coefficients in the absence of an electric field are in the order $\text{PC} \gg \text{TFSI} > \text{Li}$, and this order is retained only at low voltages. Since Li/Li electrodes were used, fast-induced migration of the lithium ions in the electrolyte is expected. Actually, the lithium drift migration is enhanced by the applied voltage, while the effects on TFSI are much smaller and PC diffusion was little influenced. The anion necessarily drifts in the opposite direction to the lithium ion to maintain the neutrality. The induced drift migration of the PC (i.e., the averaged migration of the solvated and free molecules) was almost negligible in the present salt concentration and suggests that lithium solvation effect is negligible in the dynamic state produced by the non-blocking electrodes.

When the electric field was below 1.0 V the drift ion migration was small, even after a long t_{DC} . Above 1.5 V, an almost linear dependence of the drift velocity induced by the electric field was observed until 3.0 V. Since a linear dependence of the current density was observed for the same cell as shown in Figure 2c, the behaviors of the charged ions around the electrodes and the remote bulk may be different. Since LiTFSI in PC can form a stable interface with the lithium metal, the usage of the present solution electrolyte is a good model for studying the electrode–electrolyte relationship. The present method is useful for understanding the migration of ions and solvents near and remote to the electrodes in an electronic cell. Under static conditions, the lithium transference number $N_{\text{transference}}$ is always smaller than 0.5 for electrolytes used for lithium secondary batteries including gel and polymer electrolytes independent of the measuring methods. As shown in the present study, the dynamic lithium transport is demonstrated to be much larger than the static $N_{\text{transference}}$ under the present experimental configuration, which closely mimics that in actual electric devices. Knowledge of the dynamic lithium transport is important for designing advanced electrochemical energy storage devices for use in, for example, hybrid electric vehicles (HEVs). The present technique could provide important information for the dynamic cation and anion transport behaviors.

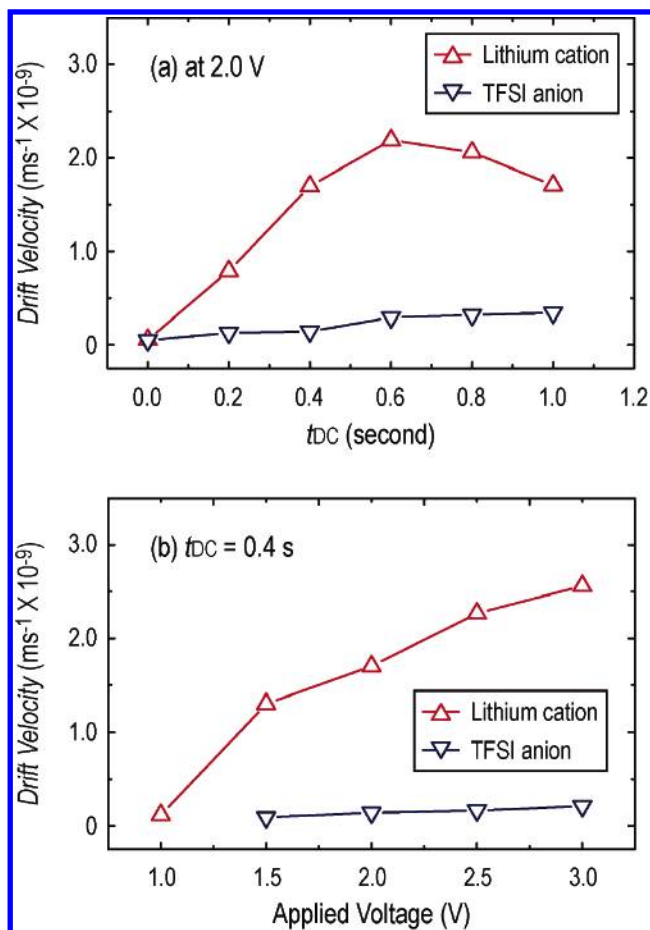


Figure 3. (a) Delay time dependence of the drift velocity of lithium ion and anion (TFSI) induced by the electric field of 2 V. Panel (b) shows the electric field dependence of the drift velocities for the lithium ion and anion TFSI measured at $t_{DC} = 0.4$ s. To observe the individual drift diffusion coefficients, the total measuring time accompanied by the electric field become inevitably long. To prevent changes to the surface of the lithium electrodes, the delay time t_{DC} was set shorter than the time required to reach an equilibrium state. Since the solvent drift migration was negligible, the solvation effects on the lithium ion are reduced under the electric field.

At present two unresolved problems remain. First, under voltages less than 1.0 V ion drift migration was not induced in the bulk, although an electric current was produced. Second, what is the nature of PC solvation of the Li ions during the reaction with the lithium metal at the electrodes? Finally, eq 2 for the ENMR was derived under the assumption that the induced ion velocity is proportional to the applied electric field. The present results do not follow this assumption, and the ion

drift migration under the voltage is more complicated. Electrochemically it is well known that interface of the electrodes is sensitive to stability. Although exact values from the similar NMR cells could not be expected, the predominant lithium ion drift migration under a proper applied voltage will be observed by waiting a suitable period after the application of the electric field.

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Supporting Information Available: The results of the Impedance measurements are given (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry*, Vol. 1, Ionics; Plenum Press: New York, 1998.
- (2) Price, W. S. *Concepts Magn. Reson.* **1997**, 9, 299. Price, W. S. *Concepts Magn. Reson.* **1998**, 10, 197.
- (3) Johnson, C. S., Jr. *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; Wiley: New York, 1996; p 1886.
- (4) Holz, M. *Diffusion in Condensed Matter*; Heitjans, P., Karger, J., Eds.; Springer: Berlin, 2005; p 717.
- (5) Pettersson, E.; Furo, I.; Stilbes, P. *Concepts Magn. Reson.* **2004**, 22A, 61 and references therein.
- (6) Dai, H.; Zawodzinski, T. A. *J. Electroanal. Chem.* **1998**, 459, 111.
- (7) Kataoka, H.; Saito, U.; Sakai, T.; Deki, S.; Ikeda, T. *J. Phys. Chem. B* **2001**, 105, 2546.
- (8) Tarascon, J.-M.; Armand, M. *Nature* **2001**, 414, 359.
- (9) Hayamizu, K.; Aihara, Y.; Arai, S.; Garcia-Martinez, C. *J. Phys. Chem. B* **1999**, 103, 519.
- (10) Aihara, Y.; Sugimoto, K.; Price, W. S.; Hayamizu, K. *J. Chem. Phys.* **2000**, 113, 1981.
- (11) Aihara, Y.; Bando, T.; Nakagawa, H.; Yoshida, H.; Hayamizu, K.; Akiba, E.; Price, W. S. *J. Electrochem. Soc.* **2004**, 151, A119.
- (12) Tokuda, H.; Muto, S.; Hoshi, N.; Minakata, T.; Ikeda, M.; Yamamoto, F.; Watanabe, M. *Macromolecules* **2002**, 35, 1403.
- (13) Hayamizu, K.; Aihara, Y.; Arai, S.; Price, W. S. *Solid State Ionics* **1998**, 107, 1.
- (14) Edman, L.; Doeff, M. M.; Ferry, A.; Kerr, J.; Jonghe, L. C. D. *J. Phys. Chem. B* **2000**, 104, 3476.
- (15) Hayamizu, K.; Akiba, E.; Bando, T.; Aihara, Y.; Price, W. S. *Macromolecules* **2003**, 36, 2785.
- (16) Shin, J. H.; Passerini, S. *J. Electrochem. Soc.* **2004**, 151, A238.
- (17) Croce, F.; Appetecchi, G. B.; Scrosati, B. *Nature* **1998**, 394, 456.
- (18) Croce, F.; Curini, R.; Martinelli, A.; Persi, L.; Ronci, L.; Scrosati, B.; Caminiti, R. *J. Phys. Chem. B* **1999**, 103, 10632.
- (19) Hayamizu, K.; Aihara, Y.; Price, W. S. *J. Chem. Phys.* **2000**, 113, 4785.
- (20) Gadjourova, Z.; Andreev, Y. G.; Tunstall, D. P.; Bruce, P. G. *Nature* **2001**, 412, 520.
- (21) Mao, G.; Perea, R. F.; Howells, W. S.; Price, D. L.; Saboungi, M.-L. *Nature* **2000**, 405, 163.
- (22) Seki, S.; Susan, M. A. B. H.; Kaneko, T.; Tokuda, H.; Noda, A.; Watanabe, M. *J. Phys. Chem. B* **2005**, 109, 3886.
- (23) Stejskal, E.O.; Tanner, J. E. *J. Chem. Phys.* **1965**, 42, 288.