

Characterizing Interactions of Ionic Liquid Based Electrolytes with Electrospun Gas Diffusion Electrode Frameworks by ^1H PFG NMR

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Abstract

Pulsed field gradient (PFG) ^1H NMR was used to characterize the mobility of ionic liquid cations in porous gas diffusion electrode (GDE) frameworks for metal–air electrochemical systems. The carbon GDE frameworks were produced by electrospinning. It was found that the motion of ionic liquids in the highly porous hosts is more complex than what is commonly exhibited by conventional fluids, which makes a multimodal investigation essential for an adequate description of mobility and wetting of GDEs. Observed NMR diffraction-like patterns cannot be linked to the tortuosity limit but may serve as a proxy for structural features in the fibrous material. While the observed data were interpreted using standard theoretical models, alternative explanations and causes for artifacts are discussed.

Keywords

Pulsed field gradient NMR, NMR diffraction of diffusion, Gas diffusion electrode, Ionic liquid electrolyte, Battery materials

1. Introduction

Metal–air battery systems are currently widely investigated due to their two- to tenfold higher theoretical energy density compared to lithium-ion technologies [1]. The air electrode or gas diffusion electrode (GDE) that represents the cathode for this battery type uses ambient air, which leads to a fundamentally lighter battery. A GDE basically consists of a catalyst with sufficient electrocatalytic activity for the oxygen reduction reaction (ORR) during discharge and oxygen evolution reaction (OER) during charge, a conductive additive and a binder to glue the materials. As conductive additive, carbon materials are commonly used in GDE's due to their wide potential window with respect to electrochemical oxidation and reduction and an electrocatalytic activity for a wide range of redox reactions [2].

Aqueous electrolytes are vulnerable to CO_2 , evaporation and atmospheric moisture what decreases battery performance. Ionic liquid (IL) are considered as electrolytes to overcome this issues. IL's are organic salts that are usually liquid at room temperature. They can be advantageous over common aqueous electrolytes since they are non-volatile, do not suffer from pH-altering CO_2 uptake and are considered as “green solvents” [3].



Over the last decade, electrospinning has been established as a versatile technique to prepare uniform fibrous materials with very thin and long fibers for energy and environmental applications [4]. Unlike melt spinning or solution-based direct spinning techniques, the deposited fibers are a few nanometers to several micrometers in diameter due to the high degree of stretching during the spinning procedure in the electric field [5]. This technology enables the preparation of high surface area materials, used e.g. for fuel cells [6] and batteries [7], where additives such as catalysts can be selectively incorporated into the fiber surface during the spinning process. Therefore, this class of materials is promising for the application as GDE in metal–air batteries [8].

NMR has proven to be a powerful tool to study diffusion and exchange processes [9]. In recent years this method has gained attention in the field of battery research since everything from individual components up to complete cells can be non-invasively monitored post-mortem, in-situ or in-operando [10, 11]. Although NMR has been applied to analyze ionic liquids [12, 13], only a few studies exist where NMR was employed to investigate the mobility of neat ionic liquids [14–19] or IL confined to carbon surfaces [20, 21]. More commonly, the dynamics of IL has been studied using methods other than NMR, such as atomic force microscopy (AFM) [22] or X-ray photoelectron spectroscopy [23].

In this contribution the suitability of PFG NMR techniques to address the interactions of ionic liquids with different alkyl chain length and carbon-based GDE frameworks is investigated, since it has been shown that ion motion differs with alkyl chain length [24, 25]. The mobility of the cation is estimated qualitatively and semi-quantitatively from the measurements, and potential sources of artefacts are discussed.

2. Methods and Materials

The carbon fibers (Fig. 1) were synthesized in a two-step procedure. In a first step the initial polymer fibers were spun from a polymer solution containing dimethylformamide (DMF, Sigma Aldrich, St. Louis/USA) and 10 wt.% polyacrylonitrile (PAN, Sigma Aldrich, St. Louis/USA) under controlled ambient conditions using an electrospinning device (EC-CLI; IME technologies, Geldrop/NL). The spinning process was conducted at 60% relative humidity, a temperature of 20°C and an accelerating voltage of 20 kV. In a second step the polymer was cross-linked followed by carbonization under an inert argon gas atmosphere.

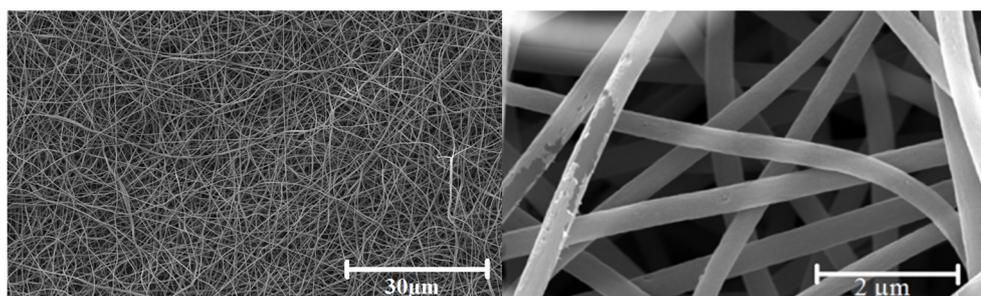


Fig. 1: SEM image of electrospun gas diffusion electrode (GDE) framework material at different magnifications. (left) Overview. (right) Closeup.

The fibre samples were fully ($c=1$) or partly ($c=1/3$) soaked with 1-Methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr₁₃ TFSI) ionic liquid (Iolitec, Heilbronn/Germany, where c is the degree of saturation of the pore space with IL). In addition, one sample was fully soaked ($c=1$) with 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr₁₄ TFSI) (Iolitec, Heilbronn/Germany). Both ionic liquid were used as received (water <500 ppm). The samples were placed in a 25 mm outer diameter glass test tube for NMR imaging (Hilgenberg, Malsfeld/Germany).

^1H PFG NMR measurements were conducted using a Bruker Avance III 14.1 T spectrometer, equipped with a Micro 2.5 gradient system capable of generating pulsed magnetic field gradients up 1.5 T m^{-1} and a MICWB40 micro imaging probe with a 25 mm ^1H quadrature insert. The sample temperature was maintained at 19°C for all measurements. The stimulated echo version of the *Stejskal and Tanner* [26] diffusion experiment was applied with a gradient pulse duration of $\delta = 8 \text{ ms}$, time between the two gradient pulses $\Delta = 14 \text{ ms}$, 500 ms recycle delay and 128 gradient steps. The raw NMR data was Fourier transformed along the transient dimension and the diffusion time distribution was obtained, where appropriate, by performing a regularized inversion using an exponential kernel without non-negativity constraint [27].

3. Results and Discussion

Fig. 2 shows the echo intensity as a function of gradient strength for Pyr₁₄ TFSI confined to the GDE framework material under fully saturated conditions. Since diffusion is restricted under confinement, the matrix structure of a porous solid affects the displacement probability [28]. For porous media showing some degree of regularity in their structure along the magnetic field gradient direction, diffusive diffraction patterns may be observed in PFG diffusion NMR experiments if the δ -dependent wavelength λ of the magnetization helix imprinted on the ^1H nuclei of the IL cations matches the structural length scale of the confining matrix [29, 30]. From these patterns the size and shape of the compartments may be assessable.

From visually examining the pores in Fig. 1 it is apparent that the GDE framework possesses a low tortuosity and exhibits no defined connected pore spaces and throats, hence it would be expected that IL motion corresponds to marginally restricted free diffusion. However, a diffusive diffraction-like pattern is evident for Pyr₁₄ TFSI, with a first diffraction minimum at $\approx 4 \mu\text{m}$, which is on the order of the dimension of the empty-space regions between the fibers. Nonetheless, the open pore space suggests that diffusive diffraction cannot be interpreted in terms of a measure for pore throat lengths.

More generally, such a diffraction-like feature could be caused by a regular pattern of spatial regions with alternately prolonged and reduced residence time for the IL. The direction of this pattern is along the axis parallel to the acceleration direction of the fiber during the electrospinning process, which corresponds to the direction of the pulsed field gradient. With $\Delta = 14 \text{ ms}$ and a self-diffusion coefficient $D_0 \approx 7 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ for the neat ionic liquid, the square root of the mean square distance of diffusive IL cation motion would be expected to be $\langle r^2 \rangle^{0.5} \approx 0.5 \mu\text{m}$. Despite the approximate nature of this calculation, it reveals a considerable discrepancy between the displacement expected in bulk IL and the apparent distance covered according to the diffraction-like minimum in Fig. 2. It points towards accelerated motion of

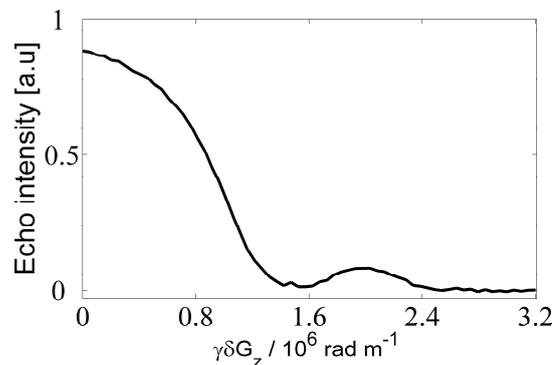


Fig. 2: Decay of the echo intensity in a ^1H PFG diffusion experiment for Pyr₁₄ TFSI (cation) electrolyte confined to electrospun carbon gas diffusion electrode framework.

the Pyr₁₄ TFSI IL in the environment of the fibrous GDE framework, which could be a macroscopic manifestation of an effect that has been characterized on a microscopic scale as a consequence of the formation of charged layers in the vicinity of carbonaceous surfaces. Inversely to classical restricted motion of a molecular liquid in a porous medium, this indicates an accelerated motion through tight regions or along intersections of fibers between the large bulk-like pockets of IL in the porous GDE framework. In other words, this would correspond to prolonged residence time in bulk-like regions and accelerated motion along the “pores”. The reason for the pronounced formation of a diffraction minimum could be the occurrence of a structural anisotropy in the GDE framework due to the two-dimensional production process of electrospun materials, where the third dimension is gained layer-by-layer, showing a different topology than the two in-plane dimensions. Further, the nature of the GDE may introduce periodic magnetic field gradients due to susceptibility differences by the fibers [31]. Note that the observation of diffraction-like phenomena in the echo intensity of a PFG NMR experiment renders the conventional interpretation of self-diffusion according to *Stejskal and Tanner* [26] impossible, even if a distribution of effective diffusion coefficients is calculated [32].

An identical experiment was conducted using Pyr₁₃ TFSI for different loading fractions of the GDE framework pore space. The self-diffusion coefficient of Pyr₁₃⁺ cations in the neat IL is similar to D_0 of Pyr₁₄⁺. However, no diffraction-like features were observed in the PFG diffusion NMR experiment, hence inversion of the data was attempted.

Fig. 3 shows the spectrally resolved distribution of the apparent diffusion coefficient D_{eff} of Pyr₁₃ TFSI cations confined to electrospun GDE framework under partially (a) and fully (b) saturated conditions, where the corresponding spectrum is given at the top of each figure. While for both samples the main signal in the diffusion dimension is consistent with self-diffusion of the neat IL, additional signal contributions show significant differences of the diffusion behavior between the two samples. For $c=1/3$, the downfield spectral region shows an unusual feature of significantly enhanced effective diffusion compared to the self-diffusion coefficient of the neat IL, i.e. $D_{\text{eff}} > D_0$. This indicates an acceleration of diffusive motion inside the porous medium over length scales of μm . Furthermore, there are a couple of regions exhibiting a sign change of the signal, which indicates exchange between two distinct environments inside the sample. In particular, such an exchange may occur between IL near the fiber surface and bulk-like IL. An explanation in accordance with these observations would be an accelerated IL cation motion close to the fiber surface. A nearly stationary film of preferentially aligned IL molecules directly on the fiber surface, which can be observed by AFM [22], may effectively act as a lubricant for IL cations within a few layers from this

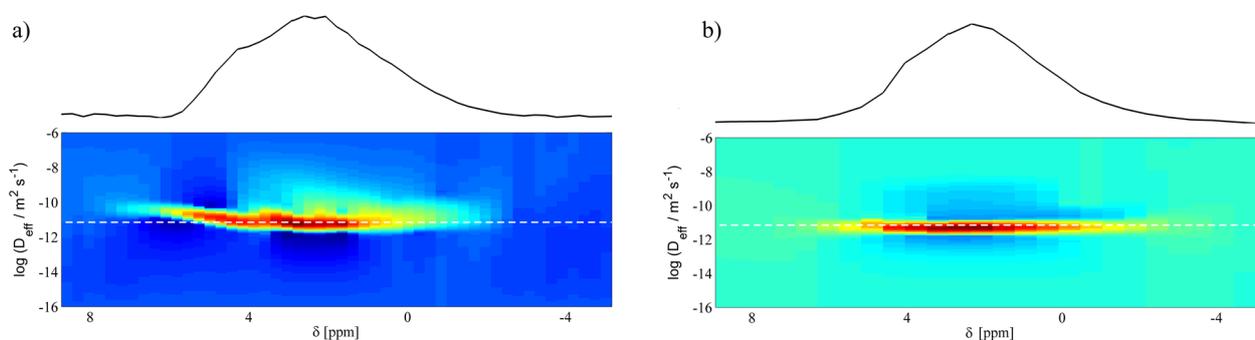


Fig. 3: Spectrally resolved diffusion coefficient distributions of Pyr₁₃ TFSI electrolyte confined to electrospun GDE framework, derived from ¹H PFG NMR measurements under a) partial ($c=1/3$) and b) full ($c=1$) saturation with IL. (top) NMR spectra. (bottom) 2D representation of spectrum vs. diffusion coefficient. The amplitudes are square root scaled with conservation of the sign to enhance weak features. The dashed white line represents the neat diffusion coefficient of Pyr₁₃ TFSI.

surface, resulting in an increased diffusion. The residence time within these layers may be prolonged by the formation of ion layering, which prevents an averaging out of these effects on the NMR timescale. Such a model would be consistent with the findings of *Perkin et al.* [33]. The $c=1$ sample shows bipolar features in the D_{eff} dimension, which are characteristic, but not a proof, for data inverted with an improper kernel. Given the similarity of D_0 for Pyr_{13}^+ and Pyr_{14}^+ in neat IL with TFSI as counterion and the structural similarities of the two cations, it is conceivable that the apparent D_{eff} distribution could be caused by an unresolved diffraction-like pattern. Therefore an interpretation of the observed features is not attempted for this sample. Nonetheless, this result shows that the dynamics inside the sample can be considerably different for even slightly different ILs and IL loadings.

Conclusions

GDE frameworks together with efficient electrolytes are key factors to improve battery performance. PFG NMR has been used to study non-invasively the cation dynamics of two ionic liquids confined to an electrospun GDE framework. The observed dynamic behavior differed distinctively from the well investigated properties of normal liquids in porous media. Different mobility regimes could be identified with relatively slow exchange between the domains despite the very open morphology of the GDE framework produced by electrospinning. The surface-directed diffusion along the fibers is expected to be of particular importance for the transport of reactive species and electrons in battery electrodes, which will be investigated systematically in the future.

In general, NMR diffusometry was found to be suitable to investigate the mobility of IL as well as, indirectly, the porous matrix of electrospun GDE framework. The motion of ionic liquids in porous hosts turned out to be more complex than what is commonly exhibited by fluids; hence a multimodal investigation will be essential for an adequate description of mobility and wetting. The directly accessible information of molecular displacement afforded by ^1H PFG NMR was invaluable to gain insight into the ionic liquid distribution and motion in porous electrodes. Nevertheless, since these materials are prone to diffraction-like diffusion behavior, common assumptions to analyze diffusion data of fluids in porous media need to be verified for this class of sample before being used for systematic sample screening.

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References

- [1] D. Linden, *Fuel and Energy Abstracts*, 1995, **36**, 265.
- [2] R. L. McCreery, *Chem. Rev.*, 2008, **108**, 2646-2687.
- [3] P. G. Jessop, *Green Chemistry*, 2011, **13**, 1391-1398.
- [4] B. Ding and J. Yu, *Electrospun nanofibers for energy and environmental applications*, Springer, 2014.
- [5] M. Simonet, N. Stingelin, J. G. Wismans, C. W. Oomens, A. Driessen-Mol and F. P. Baaijens, *Journal of Materials Chemistry B*, 2014, **2**, 305-313.
- [6] S. T. Aruna, L. S. Balaji, S. S. Kumar and B. S. Prakash, *Renewable and Sustainable Energy Reviews*, 2017, **67**, 673-682.
- [7] X. Li, Y. Chen, H. Huang, Y.-W. Mai and L. Zhou, *Energy Storage Materials*, 2016, **5**, 58-92.

- [8] G. S. Park, J.-S. Lee, S. T. Kim, S. Park and J. Cho, *Journal of Power Sources*, 2013, **243**, 267-273.
- [9] M. Schönhoff and O. Söderman, *The Journal of Physical Chemistry B*, 1997, **101**, 8237-8242.
- [10] O. Pecher, J. Carretero-González, K. J. Griffith and C. P. Grey, *Chemistry of Materials*, 2017, **29**, 213-242.
- [11] H. W. Spiess, *Macromolecules*, 2017.
- [12] H. Weingärtner, *Current Opinion in Colloid & Interface Science*, 2013, **18**, 183-189.
- [13] A.-L. Rollet and C. Bessada, in *Annual Reports on NMR Spectroscopy*, ed. A. W. Graham, Academic Press, 2013, vol. Volume 78, pp. 149-207.
- [14] M. Kunze, E. Paillard, S. Jeong, G. B. Appetecchi, M. Schönhoff, M. Winter and S. Passerini, *The Journal of Physical Chemistry C*, 2011, **115**, 19431-19436.
- [15] A. Noda, K. Hayamizu and M. Watanabe, *The Journal of Physical Chemistry B*, 2001, **105**, 4603-4610.
- [16] G. Annat, D. R. MacFarlane and M. Forsyth, *The Journal of Physical Chemistry B*, 2007, **111**, 9018-9024.
- [17] Y. Mao and K. Damodaran, *Chemical Physics*, 2014, **440**, 87-93.
- [18] A. Ordikhani Seyedlar, S. Stapf and C. Mattea, *Physical Chemistry Chemical Physics*, 2015, **17**, 1653-1659.
- [19] D. Kruk, R. Meier, A. Rachocki, A. Korpała, R. K. Singh and E. A. Rössler, *The Journal of Chemical Physics*, 2014, **140**, 244509.
- [20] A. C. Forse, J. M. Griffin, V. Presser, Y. Gogotsi and C. P. Grey, *The Journal of Physical Chemistry C*, 2014, **118**, 7508-7514.
- [21] A. C. Forse, J. M. Griffin, C. Merlet, P. M. Bayley, H. Wang, P. Simon and C. P. Grey, *Journal of the American Chemical Society*, 2015, **137**, 7231-7242.
- [22] Y. Yokota, T. Harada and K.-i. Fukui, *Chemical Communications*, 2010, **46**, 8627-8629.
- [23] T. Cremer, *Ionic liquid bulk and interface properties: electronic interaction, molecular orientation and growth characteristics*, Springer Science & Business Media, 2013.
- [24] O. Palumbo, F. Trequattrini, G. B. Appetecchi and A. Paolone, *The Journal of Physical Chemistry C*, 2017, **121**, 11129-11135.
- [25] F. Ferdeghini, Q. Berrod, J.-M. Zanotti, P. Judeinstein, V. G. Sakai, O. Czakkel, P. Fouquet and D. Constantin, *Nanoscale*, 2017, **9**, 1901-1908.
- [26] E. O. Stejskal and J. E. Tanner, *The Journal of Chemical Physics*, 1965, **42**, 288-292.
- [27] J. Granwehr and P. J. Roberts, *Journal of Chemical Theory and Computation*, 2012, **8**, 3473-3482.
- [28] P. N. Sen, *Concepts in Magnetic Resonance Part A*, 2004, **23A**, 1-21.
- [29] R. Valiullin, *Diffusion NMR of Confined Systems: Fluid Transport in Porous Solids and Heterogeneous Materials*, Royal Society of Chemistry, 2016.
- [30] P. T. Callaghan, *Translational Dynamics and Magnetic Resonance: Principles of Pulsed Gradient Spin Echo NMR*, OUP Oxford, 2011.
- [31] M. D. Hürlimann, *Journal of Magnetic Resonance*, 1998, **131**, 232-240.
- [32] G. D. J. Phillies, *Soft matter*, 2015, **11**, 580-586.
- [33] S. Perkin, *Physical Chemistry Chemical Physics*, 2012, **14**, 5052-5062.