



“Proton Conduction in Diverse Media”
Fitzwilliam College, Cambridge, 11th-12th April 2005

ABSTRACTS OF POSTER PRESENTATIONS

“Explicit Proton Transport in Hydrated Nafion”

Matthew Petersen, Gregory Voth

Department of Chemistry, University of Utah, Salt Lake City, UT 84112, USA

Solvation of the hydrated excess proton was studied in Nafion 117 through a series of molecular dynamics simulations using the multistate empirical valence bond (MS-EVB) and self-consistent iterative multistate empirical valence bond (SCI-MS-EVB) methodologies, which enable the delocalization of the excess proton through the Grotthuss hopping mechanism. The MS-EVB simulations were performed such that “classical” non-dissociable hydronium cations and a single excess proton treated with the MS-EVB methodology were at a concentration ratio of 39:1. A marked difference in the solvation structures of the classical versus MS-EVB treated (Grotthuss shuttling) excess proton species was observed. These differences are attributed to the solvent dynamics needed to transfer the cation between the solvent separated and contact pair positions about the sulphonate counterion. Sulfonate/hydronium ion pair dissociation was characterized for the MS-EVB hydronium and its delocalized excess charge, or so-called Center of Excess Charge (CEC), using the SCI-MS-EVB method. The results demonstrate that it is generally impossible to describe the low pH conditions in the hydrophilic domains of Nafion without the explicit treatment of Grotthuss delocalization.

“Molecular dynamics-EVB simulation of an excess proton in supercritical water”

Jordi Martí^{1*}, Daniel Laria², Elvira Guàrdia¹

¹*Department of Physics and Nuclear Engineering, Technical University of Catalonia, Barcelona, Spain.*

²*University of Buenos Aires and Comisión Nacional de Energía Atómica, Buenos Aires, Argentina.*

*corresponding author (email: jordi.marti@upc.edu)

Excess protons play a key role in processes such as acid-base equilibrium (pH) or charge transport in biological membranes. The importance of supercritical water (SCW) is multiple: corrosion, hydrolysis processes, oxidation of organic wastes, catalysis, etc. At ambient conditions, the responsible for proton diffusion at the molecular level is the Grotthuss mechanism: proton jumps along hydrogen-bond chains. However, hydrogen bonding in low-density SCW is weak and this fact has relevant influence on the proton transport properties like diffusion or the transfer rate.

“About the choice of the protogenic group in proton conducting separator materials for intermediate temperature fuel cells”

M. Schuster, K. D. Kreuer*, A. Noda, T. Rager and J. Maier

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany

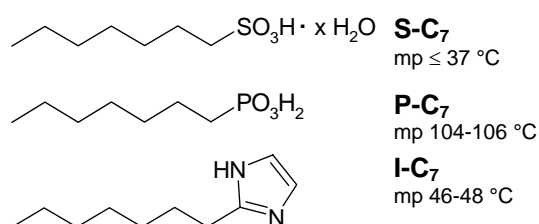
*corresponding author (email: kreuer@fkf.mpg.de)

State-of-the-art separator materials for PEM fuel cells are commonly sulfonic acid polymers, which show the required high proton conductivity only at high degrees of hydration, i.e. high relative humidities. The water solvates the acidic protons and promotes its transport, i.e. it is essential for the formation and mobility of protonic charge carriers.

But the hydration requirement of conventional membranes is the reason for at least two severe problems relevant for the use of such membranes in fuel cells: the maximum operation temperature is limited by the dew point of water and there is significant water and/or methanol "cross-over" as a result of permeation and electroosmotic drag.

Therefore one challenge in polymer electrolyte fuel cell research is to find proton conducting materials which also operate at higher temperatures and low humidification, preferentially under anhydrous conditions. Mainly three functional groups have been considered as protogenic group for fuel cell membranes: sulfonic acid groups, phosphonic acid groups [1], and nitrogen heterocycles [2-5].

In order to evaluate the suitability of these functional groups for fuel cell applications, we have prepared the model compounds S-C₇, P-C₇, I-C₇ and characterized these with respect to proton conductivity, proton diffusion coefficients, thermo-oxidative stability, water uptake, and electrochemical stability in the dry and wet state. Proton conductivity was measured by



impedance spectroscopy, diffusion coefficients were determined by frequency-resolved pulsed field gradient NMR, thermal stability was investigated by TGA-MS under 20% oxygen atmosphere, water uptake was investigated by TGA under saturated water vapor, and electrochemical stability by cyclic voltammetry.

The results suggest that the phosphonic acid group shows the most suitable combination of properties among the three functional groups for proton conduction at intermediate temperatures, including satisfactory conductivity even in the water-free state and comparatively high thermo-oxidative and electrochemical stability. A moderate uptake of water allows for reasonable conductivities even at lower temperature and may prevent condensation reactions at higher temperature [6].

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“Intermediate Temperature Proton Conducting Systems with Improved Conductivity and Stability”

H. Rößler^a, M. Schuster^a, T. Rager^a, A. Noda^a, K. D. Kreuer^{a*}, J. Maier^a, G. Scharfenberger^b, W. H. Meyer^b

^aMax-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany

^bMax-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

*corresponding author (email: kreuer@fkf.mpg.de)

The proton conductivity of polymer membranes used as separators in fuel cells strongly depends on the presence of water, which requires a complex water management and limits the maximum operation temperature to temperatures which do not significantly exceed the dew point of water (100 °C at ambient pressure). This work presents progress of a different approach for obtaining high proton conductivity in water free environments based on heterocycles (imidazole) and phosphonic acid as proton solvating functional groups:

(i) It has already been reported that heterocycles (e.g. imidazole, pyrazole or benzimidazole) show similar proton solvating properties as water and may act as proton donor and acceptor in extended hydrogen bond networks [1]. But, as opposed to water, heterocycles may be bound to a polymeric network via C-C bonds. In order to maintain the typical features of a dynamic hydrogen bond network [2], heterocycles are bound to different polymer backbones via flexible spacers (alkyl- or ethylenoxide chains) in an appropriate way. In the temperature range 100 to 200°C proton conductivities ranging from 10^{-4} to 10^{-3} S cm⁻¹ have been achieved for oligomers [3,4] and polymers [5], which is not yet sufficient for fuel cell applications. Moreover, these systems suffer from poor chemical and electrochemical stability.

(ii) Therefore, we have extended the "soft spacer concept" to the use of more amphoteric phosphonic acid bound by C-P bonds. Proton conductivities up to 5×10^{-2} S cm⁻¹ have been obtained for oligomeric systems, and cyclovoltammetry indicates a significantly improved stability against anodic oxidation.

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“Proton transport in room temperature molten salts”

M. G. Del Popolo¹, J. Kohanoff¹ and R. M. Lynden-Bell²

¹*Atomistic Simulation Centre, School of Mathematics and Physics, Queen's University Belfast, BT7 1NN, UK.*

²*University Chemical Laboratory, Lensfield Road, Cambridge University, Cambridge CB2 1EW, UK.*

Room temperature molten salts, or ionic liquids (ILs), have recently come into focus as a green alternative to traditional organic solvents [1]. Amongst the various properties of ILs, the most relevant is their low melting point concomitant with a negligible volatility. Fluidity at room temperature allows, in contrast with classical molten salts, to perform chemical reactions in them without major technical limitations [1].

Modern ionic liquids are formed by highly asymmetric organic cations paired with bulky inorganic anions. Their structure results from a balance between molecular packing and screening which in turn depends sensibly on the intermolecular interactions. In the past years some research has been performed on the structure of pure ILs both experimentally [2,3] and using computer simulations [4-6]. In particular, we have studied the structure of the ionic liquid dimethyl-imidazolium chloride ([DMIM][Cl]) by means of first principle molecular dynamics [6].

Electrostatic properties and charge dynamics are expected to play a distinctive role in chemical dynamics in molten salts, as compared with neutral solvents. Describing the behaviour of protons in ILs is relevant to understand their acid-base properties, highlighting at the same time the essential features of chemical reactivity in fluids composed solely of ions. In the present work we study the behaviour of acids in [DMIM][Cl] using first principle molecular dynamics simulations.

Hydrogen chloride (HCl) and bromide (HBr) are considered as model reactants. In both cases it is found that the proton remains strongly associated in the IL, as complex anions (HCl₂⁻ and HClBr⁻) are formed. The solvation structure, energetic and dynamics of the proton are described. Furthermore, preliminary results on the proton transfer mechanism are discussed on the ground of the free energy profile along an appropriate reaction coordinate.

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“IR spectroscopy and molecular dynamics simulation studies of the hydration of Nafion[®] electrolyte membranes”

Jérémy Chabé¹, Sylvie Neyertz², Yves Maréchal¹, Gérard Gébel¹, David Brown²

¹CEA Grenoble/DRFMC/SI3M/PCI, UMR SPRAM 5819, France.

²LMOPS, UMR 5041 CNRS Université de Savoie, France.

Polymeric Nafion[®] membranes are often used as electrolytes in fuel cell devices. These membranes consist of a perfluorinated polymer backbone with perfluorinated oligoether side chains, terminated by sulphonic acid head-groups. Extensive experimental work [1-5] has shown that the polymer chains in the hydrated membranes organize themselves into structures having different characteristic lengths scales, although the origins of this phenomenon at the molecular level are not fully understood. The long-term aim of this work is thus to understand the interactions between the polymer matrix and water that give rise to the structural organization and transport mechanisms of protons. To achieve this aim, we use molecular dynamics (MD) to build a molecular structure of the Nafion[®] membrane and infrared spectroscopy to study experimentally the hydration mechanisms inside the membrane.

In this poster, some preliminary molecular modelling work using a generic force field to represent very small perfluoroalkanes with side chains will be presented. The possible interactions between the water molecules and the sulphonic acid head-groups will be discussed taking into account what has been shown by previous studies [6-9].

Experimentally, infrared spectroscopy allows us to study the behaviour of the membrane with the extent of hydration. Most previous studies have provided results that were qualitative [10-14]. The transformation of the sulphonic acid group into a sulphonate ion takes place at very low levels of hydration. As water content increases, clusters of water and ions are created. In the work presented here, we give results of a more quantitative analysis of the IR spectra [15-16]. In particular, we can analyse the interactions of the water molecule with the ions and the polymer in terms of hydrogen bonds. Our ultimate aim is to link these results to the molecular dynamics simulations in order to understand the hydration mechanisms.

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“Microporous sulfonated poly(ether ether ketone) membranes and their composites with zirconium phosphate”

Frédéric Grasset, Deborah J. Jones and Jacques Rozière

Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, UMR CNRS 5072, Université Montpellier II, France.

Operation of PEMFC at temperatures above 100 °C (limitation of Nafion type membranes) is receiving world-wide attention. Advantages include simplification of the thermal and humidification sub-systems, improved resistance to CO poisoning and increased electrode kinetics. At this temperature, high proton conductivity of sulfonated polymer membranes is only maintained if the degree of hydration is conserved. At high degrees of hydration and high temperature however, sulfonated polymer membranes undergo significant swelling, and the mechanical fatigue introduced by cyclical changes in dimension between dry and wet states accelerates membrane ageing and precipitates failure. We have developed a novel sulfonated poly(ether ether ketone) microporous membrane morphology that is dimensionally stable. Unlike previous reports of composite membranes based on porous structures in which the porous membrane provides mechanical strength and the pore-filling component confers proton conduction properties (e.g. Gore-type membranes), in the present case microporous sPEEK is proton conducting and the pore-filling inorganic or organic phase provides both mechanical reinforcement and enhances the conduction properties.

“Multilayer membranes for H₂/O₂ and direct methanol fuel cell application”

Jennifer Peron, Mathieu Marrony[‡], Frédéric Grasset, Deborah J. Jones, Jacques Rozière
Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques - UMR CNRS 5072 - Université Montpellier 2 – France

[‡] *Current address: EIfER, Emmy Noether Strasse 11, D-76131 Karlsruhe, Germany*

The proton exchange membrane (PEM) is a vital part of the fuel cell, which performs two basic functions: separation of the fuel and the oxidant and proton transport from anode to cathode. For applicability in a fuel cell, PEM must have high conductivity, low reactant permeation in both dry and humidified conditions, and be thermally and chemically stable under fuel cell operation conditions.

This work reports the preparation of multilayer membranes with the aim of increasing chemical and mechanical stability, reducing membrane swelling, improving the water management in the membrane by favouring the back diffusion of water and reducing the permeability to methanol.

Multilayer membranes presenting a gradient of ion exchange capacity can be manufactured using successive casting steps. These materials show good mechanical properties, with no tendency to delaminate even after extended use in fuel cells. They are self-humidifying and can achieve good performance at temperature higher than 100°C even in conditions of no humidification. In DMFC application they help to reduce methanol crossover. Further work is required to optimise the properties and to understand the influence of membrane manufacturing conditions on the fuel cell performance and on methanol blocking properties.

“Multiscale modelling of membrane materials for fuel cell applications”

James Elliott¹, Stephen Paddison²

¹*Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, CB2 3QZ, UK.*

²*Departments of Chemistry and Materials Science, University of Alabama in Huntsville, Alabama 35899, USA.*

A detailed physical understanding of the mechanisms of proton conduction in polymer electrolyte membranes is crucial in designing novel materials that will function efficiently in primary fuel cells involving direct oxidation of hydrogen or hydrocarbons. In particular, the production of membranes that will function at elevated temperatures, above the boiling point of bulk water, whilst still maintaining acceptably high levels of conductivity is extremely desirable. This poster describes an EPSRC-funded project (GR/S80455/01) at Cambridge, which seeks to understand the fundamental mechanisms of such ion transport using quantum mechanical computer simulations of ion transport, embedded within a classical molecular mechanics model of the polymer membrane. The molecular mechanisms of proton transport are complex, but two main possibilities are recognised. The first of those possibilities is that excess protons use water molecules as ‘vehicles’ (convection-like) and the second possibility is structural diffusion or “Grotthuss” mechanisms, in which protons hop through a network of water molecules (conduction-like). We will describe preliminary simulation work using a combination of DL_POLY and Gaussion03 to model proton transport in the most commonly used types of perfluorinated ionomer membranes (those chemically similar to Nafion[®]), and try to draw some speculative conclusions as to what are the most important structural features that impact on proton conductivity.

“Proton dynamics in hydrated acceptor-doped BaZrO₃”

Dirk Wilmer, Stefan Janssen, Klaus-Dieter Kreuer, Tilo Seydel

Universität Münster, Institute of Physical Chemistry, Corrensstr. 30, 48149 Münster, Germany

We report results of several quasi-elastic neutron scattering experiments on proton-conducting hydrated acceptor-doped barium zirconates. Quasi-elastic contributions to the spectra have been detected at different resolutions, i.e., in both time-of-flight and backscattering experiments. Our data typically show little Q -dependence in their line width and weak thermal activation which indicates that they mainly reflect the localized dynamics of the protons in these materials.

“Proton transfer in water and at the liquid-vapor interface: a combined *ab initio* and multi-state EVB molecular dynamics approach”

Giuseppe Brancato,¹ Hee-Seung Lee² and Mark E. Tuckerman³

¹*Dipartimento di Chimica, Università Federico II, Complesso Universitario Monte S. Angelo, Via Cintia, I-80126 Napoli, Italy. Email: brancato@caspur.it.*

²*Department of Chemistry, New York University, New York, New York 10003.*

³*Department of Chemistry and Courant Institute of Mathematical Sciences, New York University, New York, New York 10003.*

Proton transport in liquid water and aqueous solutions is particularly interesting due to its anomalously high mobility compared to other simple ions. It has been shown that the hydrated proton forms a “structural defect” in the water hydrogen-bond network,¹ which can rapidly diffuse, according to the Grotthuss mechanism, through the formation and disruption of the so-called Eigen (H_9O_4^+) and Zundel (H_5O_2^+) complexes. This simple picture is complicated somewhat by nuclear quantum effects, which suggest that the H_9O_4^+ and H_5O_2^+ complexes are actually ideal limiting forms of a fluctuational defect that can delocalize over several hydrogen bonds.¹ Moreover, the reduced coordination number of the hydronium ion (c.n. = 3) compared to bulk water, which is typically tetra-coordinated, along with its ability to form three strong hydrogen bonds provide the H_3O^+ species with an amphiphilic character.² As a result, protons prefer to stay in proximity of the liquid surface rather than being dissolved in the interior and such a behavior could have important consequences on the chemistry at the interface.

In this work,^{3,4} we propose a combined *ab initio*/EVB molecular dynamics approach, where the first-principle dynamics is used to obtain important information related with the electronic density distribution and, along with other high level quantum calculations and experimental data, allows the parameterization of a classical force field required by the EVB model. To this end, we introduce a multi-state EVB model³ that incorporates solvent polarization via the widely used induced point dipole approach. In the present model, the induced dipoles are determined for each valence bond state, a condition for consistency with the EVB methodology. In addition, an effective potential surface based on a path integral calculation is employed as a means of including nuclear quantum effects in a simple and computationally efficient manner. The model is shown to reproduce the geometries and energetics of small protonated water clusters accurately compared with high level *ab initio* calculations. It is then applied to proton transport in liquid water, where it is shown to yield an overall proton diffusion constant of $8.3 \pm 1.5 \cdot 10^{-5} \text{ cm}^2/\text{s}$ compared to the experimental value of $9.3 \cdot 10^{-5} \text{ cm}^2/\text{s}$, and at the aqueous liquid-vapor interface.⁴ In addition, the model faithfully reproduces the picture of a fluctuational structural defect as predicted by the *ab initio* path integral calculations of Ref. 1.

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