

# Atomistic simulation of protic ionic liquid as novel fuel cell electrolytes

Yingzhen Chen, Christian Rodenbücher, Federico Parisi, Klaus Wippermann,  
Piotr Kowalski, Carsten Korte  
Forschungszentrum Jülich, Institute of Energy and Climate Research  
52425 Jülich, Germany  
y.chen@fz-juelich.de

Protic ionic liquids are promising candidates as novel electrolytes for fuel cells operable above 100 °C [1-2]. A molecular level understanding of electrochemical processes at the electrode-electrolyte interface is crucial to improve ionic liquid-based electrolytes for fuel cell applications. The interface between proton conducting ionic liquids and a catalytic electrode is being studied by electrochemical methods in combination with vibrational spectroscopy and atomistic modeling. The vibrational spectroscopy is able to provide insights into the molecular structure and interactions in ionic liquids [3]. The density functional theory (DFT) and molecular dynamics simulations (MD) were employed to interpret the experimental spectra. Such a combination of experiment and simulations contributes to development of interfacial physicochemical models.

We selected the protic ionic liquid diethylmethylammonium triflate [Dema][TfO] as a model electrolyte. The nine most probable conformations of [Dema]<sup>+</sup> cation were evaluated by DFT calculations (Fig. 1(a)). The calculations show that [Dema]<sup>+</sup> (g2g2) is the most stable conformer, while the [Dema]<sup>+</sup> (tt) structure should be unstable. The structure of [Dema][TfO] in the bulk phase and at the interface to a Pt electrode was simulated by MD. Analyzing the simulated dihedral angles of the molecules, we concluded that the cation adopts different conformations in the liquid (Fig. 1(b)). Nearly 50 % of the cations adopt the (g1g2/g2g1) conformation, whereas (g2g2) conformation is observed only in about a quarter of cation. The results suggest that the most frequent conformation in the bulk structure of the liquid is not the [Dema]<sup>+</sup> (g2g2) as conformational calculations of an isolated cation suggests (Fig. 1(a)), indicating that the interactions in ionic liquid stabilize a configuration which is less stable as an isolated species. DFT calculations performed on small ionic liquids models (4–8 ion pairs/supercell) were employed in computation of IR spectra. Only computing a liquid vs. isolated species, a very good match to the experimental spectrum was obtain, which is even excellent in the low-frequency region. This indicates that computing ionic liquid as a continuous medium is essential for realistic description of the considered electrolytes.

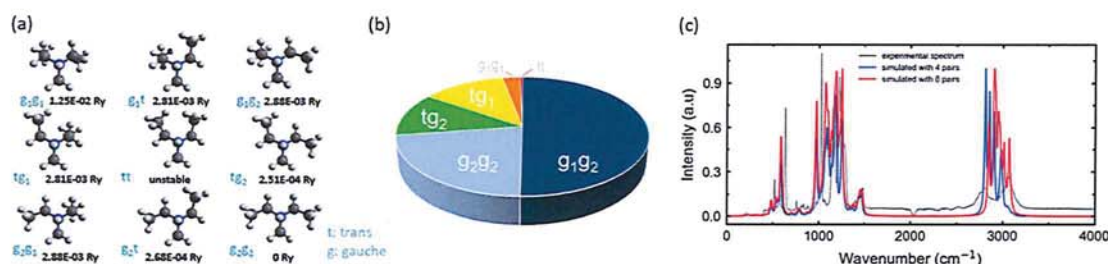


Fig. 1 (a) The conformations of the isolated [Dema]<sup>+</sup> cation with the calculated energy relative to the energy of the g2g2 conformation. (b) Conformation analysis of the [Dema][TfO] bulk phase simulated by 200 ion pairs using MD. (c) Comparison between the experimental infrared spectrum and the spectra simulated for periodic cells consisting of 4 and 8 ion pairs.

1. K. Wippermann, Y. Suo, C Korte. Oxygen Reduction Reaction Kinetics on Pt in Mixtures of Proton-Conducting Ionic Liquids and Water: The Influence of Cation Acidity. *J. Phys. Chem. C*. 2021, 125, 4423–4435.
2. H. Hou, H.M. Schütz, J. Giffin, K. Wippermann, X. Gao, A. Mariani, S. Passerini, C. Korte, Acidic Ionic Liquids Enabling Intermediate Temperature Operation Fuel Cells, *ACS Appl. Mater. Interfaces* 13 (7) (2021) 8370–8382,
3. Y. Chen, M. Endres, J. Giffin, C. Korte. Investigation of the protolytic equilibrium of a highly Brønsted acidic ionic liquid and residual water using Raman spectroscopy. *Journal of Molecular Liquids*. 2022, 345, 117796.