

Research Project #18

Physicochemical investigations of the electric double layer of protic ionic liquids as novel electrolytes for high-temperature polymer fuel and electrolysis cells (IET-4 & INW-1)

Polymer fuel cells and electrolysis cells are pivotal technologies for clean power generation and green hydrogen production. Yet their performance and durability continue to be constrained by the low to moderate operating temperatures required by conventional polymer electrolytes and aqueous environments. Typical operation below 80 °C limits reaction kinetics, increases susceptibility to catalyst poisoning, imposes strict humidification control, and reduces overall system robustness. Overcoming these temperature constraints is therefore essential for enabling more efficient and reliable electrochemical devices.

At IET-4 and INW-1, we investigate the fundamental physicochemical properties of protic ionic liquids (PILs) as promising electrolytes for future intermediate and high-temperature fuel and electrolysis cells (100-180 °C). Their intrinsic thermal stability, negligible vapor pressure, and non-flammability allow PILs to function well beyond the temperature limits of water-based electrolytes. When incorporated into polymer fuel cells or electrolysis cells as proton-conducting electrolytes embedded in a polymer matrix, PILs can enable high-temperature operation, which would increase the overall system efficiency and thus reduce the costs of fuel and electrolysis cells [1,2].

A key factor in realizing these advantages lies in understanding and rationally engineering the electric double layer (EDL) that forms between ILs and Pt electrodes. PILs create highly ordered, ion-rich interfacial layers that differ radically from those formed in traditional proton-exchange environments [3]. These structured EDLs govern charge distribution, adsorption processes, and the activation barriers of reactions central to fuel-cell and electrolysis performance. At elevated temperatures, changes in PIL mobility, water content, and interfacial structuring can significantly influence the rates of hydrogen oxidation, oxygen reduction, and water-splitting reactions on Pt.

Despite the promise of ILs for high-temperature operation, fundamental questions remain unresolved. What is the EDL structure on the nanoscale? How is it influenced by changes in water content and electric potential? Is there a preferential tendency for blocking catalytically active sites of specific anion-cation combinations? And, importantly, how does the structure of the EDL influence the relevant electrochemical processes at the catalyst interface?

This project aims to elucidate the EDL formed between (P)ILs and Pt electrodes in model cells combining electrochemical methods with *in situ* Raman spectroscopy and X-ray diffractometry/reflectometry (XRD/XRR) [4,5]. The study focusses on a systematic selection of ILs that vary in cation type, anion chemistry, hydrophobicity, acidity and thus in proton availability. Pt electrodes—polycrystalline disks, (ordered) thin films, or single crystals—are prepared with high surface cleanliness to minimize structural ambiguities. These electrodes are incorporated into customized electrochemical cells equipped with optical and X-ray transparent windows as well as precise temperature and atmosphere control to allow operation from room temperature to the target operation temperatures above 100 °C.

Baseline electrochemical characterization using cyclic voltammetry and impedance spectroscopy provides an initial fingerprint of IL–Pt interactions by identifying ion adsorption features, potential stability windows, and temperature-dependent changes in interfacial capacitance. These data guide the subsequent spectroscopic measurements. *In situ* Raman spectroscopy is then used to probe molecular-level interactions in the EDL, beginning with bulk IL characterization to establish reference vibrational signatures associated with ion pairing, hydrogen bonding, and structural order. Potential-controlled *in situ* Raman measurements at the Pt surface reveal how IL ions reorganize in response to electrode polarization, including changes in adsorption, coordination, and formation of an ordered structure based on anion-cation

layering. Surface enhanced Raman spectroscopy (SERS) based on the use of plasmon active nanoparticles will be employed to differentiate vibrational signatures of the interface from the bulk.

Complementing Raman spectroscopy, *in situ* XRR is employed to resolve the spatial structure and ordering of ILs near the Pt surface. Initial bulk XRD measurements identify intermolecular interactions and the structure of solvation shells. Surface-sensitive XRR measurements then map interfacial layering, ion stratification, and molecular orientation within the first few nanometres above the Pt electrode (i.e., within the EDL). By applying potentials during experiments, the experiments monitor how electrochemical polarization compresses or reorganizes near-surface ordering.

The final phase integrates the complementary experimental measurements with theoretical models obtained by molecular dynamics (MD) and density functional theory (DFT) to reveal correlations between PIL chemistry, EDL structure, and electrochemical performance. Based on these findings, a model will be established predicting the most promising PIL composition to be used in test cells after embedding in a thermally stable polymer.

The project will be conducted at the state-of-the-art experimental research facilities of Forschungszentrum Jülich and large scale research facilities such as synchrotrons ERSF and PETRA III. The dissertation research will be conducted in close collaboration with internal project partners of various institute on the campus and the RWTH Aachen University as well as with leading research groups in electrocatalysis and physical chemistry in Europe, South Korea and South Africa.

The specific tasks of the project are:

- to employ cutting-edge nanoscale experimental methods for the investigation of the EDL of PILs
- to develop dedicated *in situ* model cells for Raman spectroscopy and XRR
- to evaluate the applicability of *ab initio* models for the description of electrochemical reactions
- to predict optimized electrolyte compositions for efficient high-temperature PEM fuel and electrolysis cells
- to effectively collaborate with the internal and external partners.

Location of the HITEC Fellow	Forschungszentrum Jülich, Institute of Energy Technologies - Electrochemical Process Engineering (IET-4), Physicochemical lab (PCL), Director: Prof. Dr. Ralf Peters https://www.fz-juelich.de/en/iet/iet-4
Partners of the HITEC Project	Forschungszentrum Jülich, Institute for a Sustainable Hydrogen Economy - Catalytic Interfaces for Chemical Hydrogen Storage (INW-1), Director: Prof. Dr. Hans-Georg Steinrück https://www.fz-juelich.de/de/inw/unsere-bereiche/inw-1
Specific requirements	M.Sc. in Physics, Chemistry or in related disciplines
For project specific questions please contact	Dr. Christian Rodenbücher, IET-4, c.rodenbuecher@fz-juelich.de

1. Wippermann, K.; Giffin, J.; Kuhri, S.; Lehnert, W.; Korte, C. The influence of water content in a proton-conducting ionic liquid on the double layer properties of the Pt/PIL interface. *Physical Chemistry Chemical Physics* **2017**, *19*, 24706–24723, doi:10.1039/C7CP04003B.
2. Chen, Y.; Wippermann, K.; Rodenbücher, C.; Suo, Y.; Korte, C. Impedance Analysis of Capacitive and Faradaic Processes in the Pt/[Dema][TfO] Interface. *ACS Appl. Mater. Interfaces* **2024**, *16*, 5278–5285, doi:10.1021/acsami.3c15465.

3. Rodenbücher, C.; Chen, Y.; Wippermann, K.; Kowalski, P.M.; Giesen, M.; Mayer, D.; Hausen, F.; Korte, C. The Structure of the Electric Double Layer of the Protic Ionic Liquid [Dema][TfO] Analyzed by Atomic Force Spectroscopy. *Int. J. Mol. Sci.* **2021**, *22*, 12653, doi:10.3390/ijms222312653.
4. Steinrück, H.-G.; Cao, C.; Tsao, Y.; Takacs, C.J.; Konovalov, O.; Vatamanu, J.; Borodin, O.; Toney, M.F. The nanoscale structure of the electrolyte–metal oxide interface. *Energy Environ. Sci.* **2018**, *11*, 594–602, doi:10.1039/C7EE02724A.
5. Horowitz, Y.; Steinrück, H.-G.; Han, H.-L.; Cao, C.; Abate, I.I.; Tsao, Y.; Toney, M.F.; Somorjai, G.A. Fluoroethylene Carbonate Induces Ordered Electrolyte Interface on Silicon and Sapphire Surfaces as Revealed by Sum Frequency Generation Vibrational Spectroscopy and X-ray Reflectivity. *Nano Lett.* **2018**, *18*, 2105–2111, doi:10.1021/acs.nanolett.8b00298.