ELECTROCATALYSIS IN SOLID ACID FUEL CELLS

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Mary WC Louie

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Abstract

Solid state electrochemical reactions play a crucial role in many energy conversion devices, yet the pathways of many reactions remain unknown. The elusiveness of the reaction mechanisms is due, in part, to the complexity of electrochemical reactions; because electrochemical reactions require the interaction of many species (e.g., ions, electrons, and adsorbates) across multiple phases (e.g., electrolyte, catalyst, and gas phases), elucidation of the reaction pathway can quickly become complicated. In this work, we develop and utilize model catalyst | electrolyte systems, that is, structures of reduced complexity, to study electrode reactions in solid acid fuel cells which operate at intermediate temperatures of ~ 250 ºC. We employ AC impedance spectroscopy to explore the reaction pathway for hydrogen electro-oxidation over Pt thin films sputter-deposited atop the proton-conducting solid acid electrolyte CsH_2PO_4. We observed that hydrogen electro-oxidation occurs by diffusion of hydrogen through Pt, taking advantage of the entire Pt | CsH_2PO_4 interfacial area rather than being confined to the triple-phase sites. This insight opens up new avenues for developing high performance electrodes with low Pt loadings by eliminating the requirement that Pt-based electrodes be comprised of high triple-phase site densities long considered to be critical for Pt electrocatalysis. Indeed, even for flat, planar electrodes of very thin Pt films, we obtained a Pt utilization that is significantly higher than in typical composite electrodes.

We also demonstrate the efficacy of a new tool for probing the spatial heterogeneity of electrochemical reactions at the metal | electrolyte interface. We characterized oxygen electro-reduction kinetics at the nanoscale Pt | $CsHSO_4$ interface at ~ 150 ºC using conducting atomic force microscopy in conjunction with cyclic

voltammetry and AC impedance spectroscopy. Not only did we find the electrochemical activity for oxygen electro-reduction to vary dramatically across the electrolyte surface but the current-voltage data, when analyzed in the Butler-Volmer framework, exhibited a strong counter-correlation between two key kinetic parameters, the exchange coefficient and exchange current. Specifically, the exchange current spanned five orders of magnitude while the exchange coefficient ranged between 0.1 and 0.6. Such a correlation has not been observed before and points to the power of atomic force microscopy for electrochemical characterization at electrolyte | metal | gas boundaries in general.

As reduction in microstructural complexity is a key advantage in model electrode | electrolyte systems, we also sought to understand the bulk properties of solid acid compounds, specifically, the relationship between microstructure and the superprotonic phase transition, the latter of which lends solid acid compounds their high proton conductivities at intermediate temperatures. We found a correlation between phase transformation hysteresis and crystallographic compatibility of the high- and low-temperature phases of the $Cs_{1-x}Rb_xH_2PO_4$ solid solution series. Therefore, it is to be expected that hysteresis, and therefore microcrack formation, can be minimized during phase transformation via the principle of crystallographic compatibility. This is confirmed in single crystals of $CsHSO_4$, which was found to have higher crystallographic compatibility, lower hysteresis, and significantly fewer microcracks formed during phase transition compared to CsH_2PO_4. The apparent applicability of the theory of crystallographic compatibility implies a new tool for identifying solid acid compounds with suitable microstructures for fuel cell application and for model electrode | electrolyte systems.

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List of Acronyms

ACIS	alternating current impedance spectroscopy
AFC	alkali fuel cell
AFM	atomic force microscopy
BKHP	barium potassium hydrogen phosphate, $Ba_{3-x}K_xH_x(PO_4)_2$
CDP	cesium dihydrogen phosphate, CsH_2PO_4
CHS	cesium hydrogen sulfate, $CsHSO_4$
CRDPn	cesium rubidium dihydrogen phosphate, $Cs_{1-x}Rb_xH_2PO_4$, where $n = 100x$
CV	cyclic voltammetry
dFLW	distributed finite-length Warburg
EDS	energy dispersive spectroscopy
FRA	frequency response analyzer
MCFC	molten carbonate fuel cell
OCV	open-circuit voltage
PAFC	phosphoric acid fuel cell
RMS	root mean square
SAFC	solid acid fuel cell
PEMFC	polymer electrolyte membrane or proton exchange membrane fuel cell
SEM	scanning electron microscopy
SOFC	solid oxide fuel cell
XRD	X-ray diffraction