Supporting Information for "Ruthenium as a CO-Tolerant Hydrogen Oxidation Catalyst for Solid Acid Fuel Cells"†

Alexander B. Papandrew,*[a] Robert W. Atkinson III,[a] Raymond R. Unocic,[b] and Thomas A. Zawodzinski, Jr.[a,c]

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 200X
DOI: 10.1039/b000000x

1 X-ray Absorption Data

X-ray absorption (XAS) data were acquired at beamline X11A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Spectra were obtained in transmission mode at the Ru K edge, using a Si(111) double crystal monochromator and gas ionization chambers for beam intensity monitoring. A 325 mesh Ru powder was used as a reference standard. All measurements were conducted at room temperature in air. Data analysis was performed using the iXAFS software suite. EXAFS fitting was performed for the first coordination shell for a k range from 2-12 $Å^{-1}$. Table 1 summarizes the parameters derived from the fits to the experimental data. Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. Data are shown in Figure 1 and Figure 2 below.

Table 1 EXAFS parameters derived from fitting XAS data

Sample	Shell	N	R [Å]	σ^2 [$Å^2$]	ΔE_0 [eV]	R factor
Ru standard	R_{Ru-Ru}	12	2.68 ± 0.003	0.004	0.65	0.02
Ru/XC72	R_{Ru-Ru}	7.1 ± 1.8	2.695 ± 0.01	0.009	-7.9	0.04
	R_{Ru-O}	3.3 ± 1.9	1.99 ± 0.02	0.01	-8.6	

2 Polarization Data Before Correction for Membrane iR_Ω

Electrochemical cell testing was conducted at 250 °C with gases hydrated to a dew point of 73 °C to 75 °C (approximately 0.35 bar water partial pressure). Anodes were supplied either ultrahigh purity H_2 or simulated propane reformate with a composition of 43% H_2, 37% N_2, 10% CO, 9.75% CO_2, 0.25% CH_4. All hydrogen pump cathodes were supplied ultrahigh purity H_2; all H_2-air cathodes were supplied ultrahigh-purity air. Polarization curves were recorded with a Bio-Logic VSP potentiostat by scanning the working electrode potential at 5 mV s^{-1} from the open circuit potential to an arbitrary cell potential (0.5 V for H_2 pumps, 0.2 V for H_2-air cells). Polarization data before correction for membrane ohmic resistance is shown in Figure 3 and Figure 4 below.

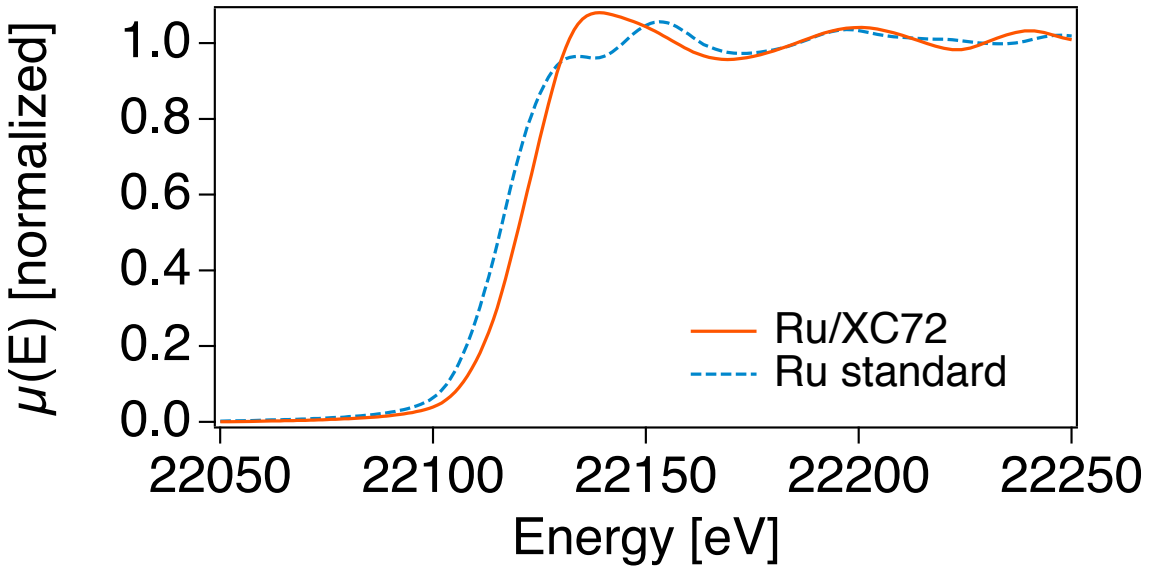

Fig. 1 Normalized XANES spectra of experimental Ru/XC72 catalyst (after 3 months of storage in air) and Ru standard. The experimental sample shows a characteristic edge shift to higher binding energies indicative of oxide formation.

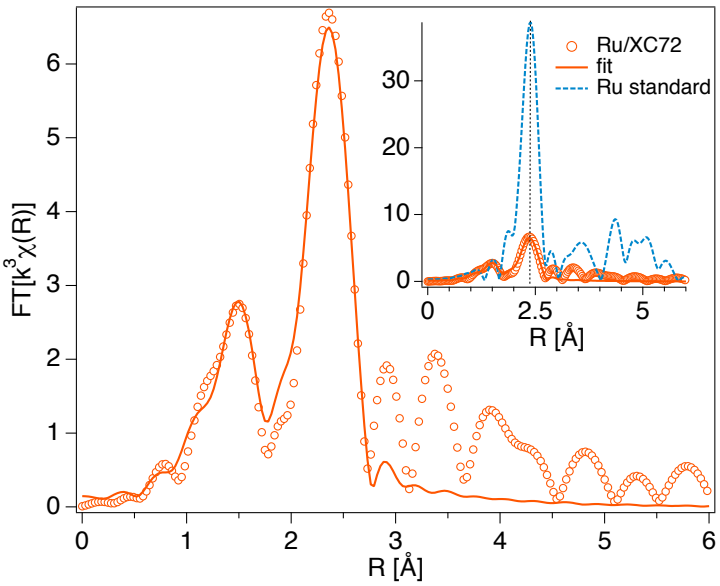

Fig. 2 EXAFS spectra of experimental Ru/XC72 catalyst (after 3 months of storage in air) including best fit to the data and Ru standard (inset). The fitting range for the experimental sample was 2-12 $Å^{-1}$.

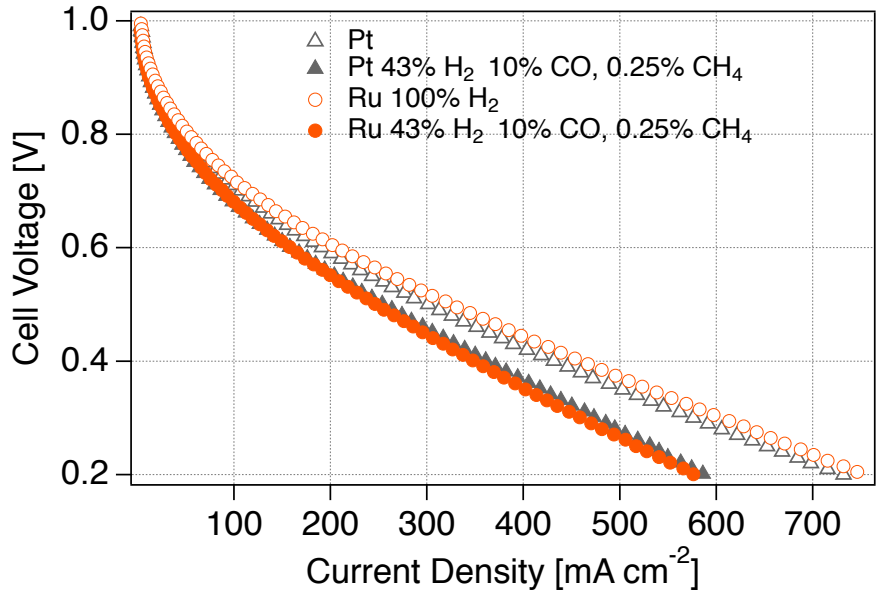

Fig. 3 Uncorrected air-breathing fuel cell polarization curves for solid acid fuel cells with Pt-based or Ru-based composite anodes acquired at 250 °C and 75 °C dew point in 100% H_2 and in a simulated reformate mixture. The full composition of the gas mixtures is detailed in the text. For each cell the cathode consisted of vapor-deposited Pt:CDP with a loading of 1.75 mg_{Pt} cm^{-2}

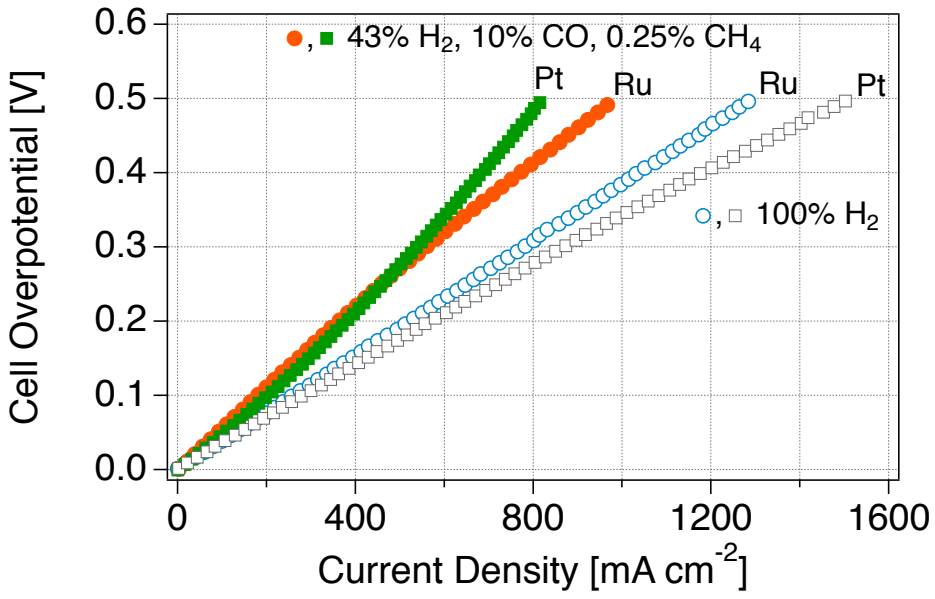

Fig. 4 Uncorrected hydrogen oxidation polarization curves for hydrogen pumps with Pt-based or Ru-based composite anodes and Pt-based cathodes acquired at 250 °C and 75 °C dew point in 100% H_2 (open markers) and in a simulated reformate mixture (43%H_2, 37% N_2, 10% CO, 9.75% CO_2, 0.25% CH_4) (filled markers).