Supplementary Information

Pt-Ru Catalyzed Hydrogen Oxidation in Alkaline Media:

Oxophilic Effect or Electronic Effect?

Ying Wang, Gongwei Wang, Guangwei Li, Bing Huang, Jing Pan,[*] Qiong Liu,

Juanjuan Han, Li Xiao, Juntao Lu, Lin Zhuang[*]

College of Chemistry and Molecular Sciences, Hubei Key Lab of Electrochemical Power

Sources, Wuhan University, Wuhan 430072, China

jpan@whu.edu.cn, lzhuang@whu.edu.cn

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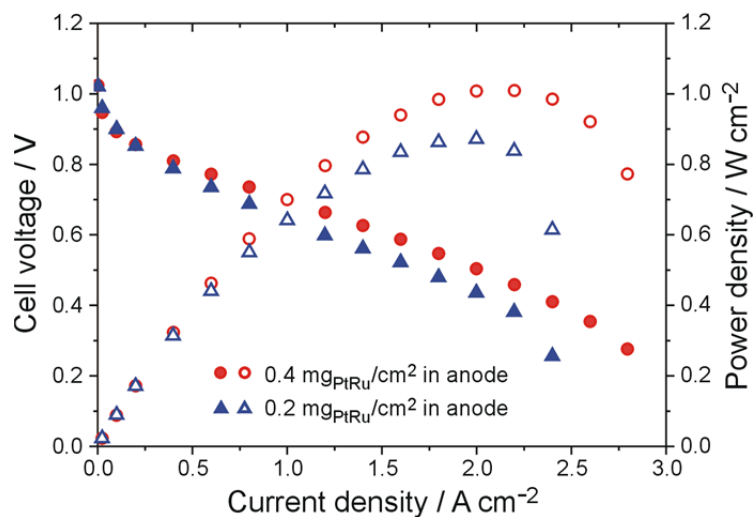
I. Supplemental Figures

Figure S1. Cell performance of APEFC using PtRu anode with different metal loadings. Operating conditions are the same as that in Figure 1.
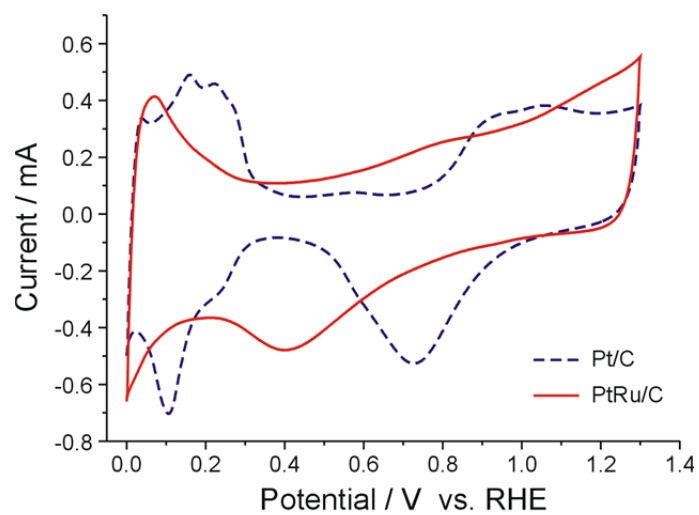

Figure S2. Cyclic voltammetry of Pt/C and PtRu/C in deaerated 0.1 M H_2SO_4 solution.

II. Experimental and Computational Details

Fuel cell tests. Pt/C or PtRu/C catalyst (60 wt% in metal content, Johnson Matthey) was mixed with certain amount of aQAPS-S$_{14}$ ionomer solution (20 wt% of ionomer and 80 wt% of catalyst) and sprayed onto each side of an aQAPS-S$_8$ membrane (50±5 μm in thickness) to produce the catalyst-coated membrane (CCM). The metal loading in both anode and cathode was controlled to be 0.4 mg/cm^2, and the electrode area was 4 cm^2. The resulting CCM was pressed between two pieces of Teflon-treated carbon paper (AvCarb GDS3250) to make the membrane electrode assembly (MEA). APEFC single cells were tested using a fuel-cell test station (850e Multi Range, Scribner) in a galvanic mode at 60°C with a backpressure 0.1 MPa on both sides. H$_2$ and O$_2$ were humidified at 60°C and fed in a flow rate 400 mL/min with a gauge backpressure 0.1 MPa. The cell voltage was recorded after the power output was stable.

Electrochemical measurements. To prepare the working electrode for usual electrochemical measurements, 2 mg of catalyst powder were dispersed ultrasonically in 0.4 mL of a Nafion (0.05 wt%) alcohol solution to form an ink. For the RDE test of HOR, the catalyst powder was mixed with a certain amount of blank XC-72 carbon in a Nafion (0.05 wt%) alcohol solution and sonicated for 1-2 h to make an ink of carbon-diluted Pt/C (metal content reduced to 3 wt%). After then, the catalyst ink were pipetted quantitatively onto a glassy carbon (GC) substrate (ϕ = 5 mm), which had been buff-polished with an alumina suspension (ϕ = 0.05 μm) prior to use. The catalyst coated electrode was dried under an infrared lamp before electrochemical tests. Electrochemical experiments were conducted on a CHI-660 potentiostat with a rotating disk electrode (RDE) system (Pine Research Instruments) at 25°C. A sheet of graphite paper was used as the counter electrode. The reference electrode was a reversible hydrogen electrode (RHE) in the same solution. The KOH (Guaranteed reagent, GR) solution was prepared using ultrapure water (18 MΩ·cm). Although it would be better to carry out electrochemical tests in a Teflon cell for alkaline electrolytes, we found that the carbon supported catalysts were not as sensitive as the planar electrode to the glass cell.

Density functional theory (DFT) calculations. DFT calculations were performed using the Vienna Atomic Simulation Package (VASP, version 5.3) within a RPBE generalized gradient approximation (GGA) to the exchange and correlation functional. A projected augmented wave (PAW) basis, along with a plane-wave kinetic energy cutoff of 408 eV, was

used throughout. For the calculations of surface and chemisorption systems, a $p(2\times2)$ surface unit cell (corresponding to 1/4 surface coverage) was used to construct a six-layer metal slab and repeated in super cell geometry with successive slabs separated by a vacuum region equivalent to six metal layers, and the Brillouin zone was sampled using a $6\times6\times1$ Monkhorst-Pack mesh. During the geometry optimization, the adsorbate layer and the top three layers of the slab were allowed to relax. The energies were converged to 1 meV per atom and ionic relaxations were allowed until the absolute value of force on each atom was below 0.02 eV/Å.