Supporting Information

A Low-loading Ru-Rich Anode Catalyst for High-Power Anion Exchange Membrane Fuel Cells

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Experimental Section

Materials:

RuCl₃.xH₂O (40-43%wt metal) 99.9%-Ru (STREM chemicals), IrCl₃.xH₂O 99.8%-Ir (STREM chemicals) and PdCl₂ 99.9%-Pd (STREM chemicals) were used as received. Silver-based catalyst (QSI-Nano® Silver with 10wt% Pd) was used as purchased.

Catalyst preparation

The RuPdIr/C catalyst was prepared by freeze-drying a dispersion of carbon (Vulcan XC-72R)-supported chloride precursors of Ru(III), Ir(III) and Pd(II), in the ratio 60%:30%:10% w/w (molar ratio of 70:18.5:11.5), followed by thermal reduction in Ar/H₂ atmosphere:

Metal salts were dissolved in hot double-distilled water. The carbon was added and the dispersion sonicated for 30 mins (Branson, 40 kHz). The sample was then freeze-dried overnight using liquid nitrogen in a VirTis BenchTop Pro freeze-dryer, operating at -105° C and ~ 50 mTorr. The dry powder (metal salts impregnated in the carbon) was collected and placed in a tube furnace, and held under a flow of Ar/H₂ (95/5 % v/v) for 2 hours at 460°C. The resulting powder was characterized and used without further treatment. The monometallic catalysts used for comparison were prepared following the same process. The freeze-drying is essential for the synthesis of well-dispersed catalyst particles with narrow particle size distribution.

Structural Characterization

The structure of the NPs was investigated using transmission electron microscope (TEM): JEOL 1400 at 120 kV. The composition of the particles was studied by electron dispersive X-ray spectroscopy (EDS) using an E-SEM Ouanta FEG 250 analyzer. Crystalline structure was resolved using a Brucker D8 Advanced X-Ray Diffractometer. High-resolution TEM images (HRTEM) and the high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM)-energy-dispersive X-ray spectroscopy (EDS) were taken on a FEI TITAN transmission electron microscope operated at 300 kV.

Electrochemical measurements

Electrode preparation and electrochemical characterization: Prior to the catalyst loading the glassy carbon electrodes (RDE electrodes) were initially polished with 0.3 μ m, followed by 0.05 μ m, alumina powder. The electrodes were then sonicated in Millipore water for 30 seconds to remove any alumina powder attached on the surface, then washed with Millipore water. The electrodes were dried and the respective catalyst inks were drop-casted onto the electrode surface to get the desired loading of the materials: 7.5 μ L of the catalyst ink solutions (1mg mL⁻¹) were drop casted on to a glassy carbon (5 mm) RDE electrode. The electrode was then kept inside a laminar flow hood while drying. All the electrochemical experiments were carried out using three-electrode system (Teflon Cell) consisting of a rotating glassy carbon working electrode along with an Hg/HgO reference electrode and a glassy carbon counter electrode. RDE linear sweep voltammetry was performed in 0.1 M KOH (Sigma-Aldrich, 99.9%) (pH = 13) with a scan rate of 10 mVs⁻¹. The electrode potential versus Hg/HgO were converted to RHE using the Nernst equation:

For CO-stripping experiments, the measurements were conducted in a 0.1 KOH argon-saturated solution with a potential scan rate of 100 mV s⁻¹ vs. a hydrogen reference electrode (Gaskatel, HydroFlex).

CO was adsorbed on the electrode by holding the potential at 0.05 V (dossing potential) for 25 min in COsaturated solution for 25 min followed by 35 min of Ar-purging. The CO-stripping was collected from 0.05 V to 1.25 V and back to 0.05 V.

Fuel Cell Testing:

5 cm² Catalyst-coated membranes (CCMs) for AEMFCs were prepared by POCELLTECH's standard methods^[1]. Catalyst inks were prepared by mixing the dispersed catalyst in a solution of a quaternary ammonium-functionalized ionomer (IEC 2.4 ± 0.2 mmol g⁻¹) and applied onto an anion exchange membrane $(IEC = 2.0 \pm 0.2 \text{ mmol g}^{-1}; \text{ s} = 43 \pm 5 \text{ mS cm}^{-1}, \text{ OH}^{-1}, \text{80}^{\circ}\text{C}/92\% \text{ RH}; \text{ t} = 30 \pm 2 \text{ mm}; \text{ liquid water uptake } 90 \pm 2 \text{ mm$ 15% at 20°C. As the catalyst for the anode electrode, carbon-supported RulrPd trimetallic nanoparticles were used at 0.2 mg cm⁻² total metal loading. The dried anode catalyst layer contained 25%w/w ionomer. A POCellTech proprietary cathode consisting of a silver-based catalyst (Quantum Sphere, 1.0 mg cm⁻² metal) containing 10% Pd was applied as the catalyst for the cathode electrode. CCMs were pre-hydrated and ion-exchanged to hydroxyl form by soaking for 10 min in 3M NaOH, followed by thorough rinsing in deionized water. There was no colour change observed after alkaline solution treatment. The CCM was then combined with gas diffusion layers (carbon fiber-based nonwovens with microporous layer, Freudenberg, Germany) to form a membrane-electrode assembly (MEA), assembled into 5 cm² test cells (Fuel Cell Technologies, AZ, USA), and sealed with Kapton (DuPont) gaskets (200 µm thick). The cell was then activated by discharge at 100 mV in humidified, CO₂-free air (1.0 standard litres per minute (sLPM), 200 kPa(abs) at dew point 77°C, 88% RH) and humidified hydrogen (0.15 sLPM, 400 kPa(abs) at dew point 65°C, 57% RH), while heating from room temperature to 80 °C. After cell temperature and current density stabilization, the cathode air was switched to O2 and polarization curves were measured at a scanning rate of 10 mVsec⁻¹ from 0.1 V to open-circuit voltage (~1.0 V), then back to 0.1 V. Cell durability was evaluated in CO₂-free air.

To check that the IV scan did not lead to elevated power densities, the FC performance was checked with a 180s galvanostatic hold at various current densities, as shown below in Figure S12.

Hydrogen pump testing: Hydrogen pump tests with 5 cm² active area MEAs were conducted at 80°C using over-humidified H_2 at 90°C dew points. The catalysts for the working electrode (WE) and for reference/counter electrode (RE/CE) were deposited on GDL's, to give gas-diffusion electrodes (GDEs)

with AEM between them functioning as solid electrolyte. To render the effects of H₂ crossover and electronic conductivity negligible, three membranes of total 90 micron were utilized between the WE and RE/CE. Low-loaded RulrPd electrodes of 0.02 mg_{metal}cm⁻² served as the WE, while high-loaded Pt electrodes of 0.4 mgPt cm⁻² served as RE/CE electrodes following the methodology described by Yan et al.^[2] This asymmetric loading allows an assumption of zero overpotential at the RE/CE "pseudo-reference" electrode. H₂ was supplied to WE with the constant rate 1 sLPM at pressure 200 kPa while RE/CE H₂ flow was 0.125 sLPM at 400 kPa. Current-voltage curves were taken in potentiostatic mode with scan rate of 8 mV/s. Prior to the polarization curves, the cell was preconditioned at 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 V for 10 min each. The durability test was performed at a constant current of 0.1 A.



Figure S1. XRD pattern of Ru/C (A) and Ir/C (B)



Figure S2. (A, B & C) TEM images of Ir/C, (D) Histogram Ir/C showing an average particle size of 2.25 nm.



Figure S3. (A, B & C) TEM images of Ru/C, (D) Histogram Ru/C showing an average particle size of 2.2 nm.



Figure S4. (A, B & C) TEM images of Pt/C, (D) Histogram Pt/C showing an average particle size of 4.5 nm.



Figure S5. (A & B) TEM images of the Ag catalyst



Figure S6: (A) Comparison of non-corrected and corrected voltage profile and (B) performance in air

(Metal (Ir+Pd+Ru) Loading: 0.1mg/cm2 H₂/Air: 0.150/0.800 sLPM RH An/Ca: 57%/ 88% Cell temp.: 80°C)



Figure S7. CO stripping analysis for the ECSA calculation of different catalysts in 0.1M KOH solution









Figure S10. (A) Schematic representation of the hydrogen pump measurements. (B) Polarization curve obtained from H₂- pump measurement and (C) stability test on RuPdIr/C.

Anode	Anode	Cathode	Cathode	PPD	Total PGM	PPD/PGM	Ref.
Catalyst	Loading	Catalyst	Loading	(mWcm-2)	Loading	(Mma-1)	
	(macm ⁻²)		(macm ⁻²)		(ma cm ⁻²)	(wing)	
	(((
Pt/C	0.40	Pt/C	0.40	737	0.80	0.92	[3]
Pt/C	0.40	Pt/C	0.40	610	0.80	0.76	[4]
PtRu/C	0.40	Pt/C	0.40	600	0.80	0.75	[5]
Pt/C	0.30	Pt/C	0.30	670	0.60	1.17	[6]
PtRu/C	0.40	Pt/C	0.40	800	0.80	1.00	[7]
PtRu/C	0.67	Pt/C	0.67	1400	1.34	1.04	[8]
PtRu/C	0.69	Pt/C	0.35	1050	1.04	1.01	[9]
PtRu/C	0.11	Pt/C	0.52	900	0.63	1.43	[10]
Pt/C	0.20	Ag based	1.00	770	0.20	2.56	This study
RuPdlr/C	0.20	Ag	1.00	947	0.20	3.15	This study
		based					
RuPdlr/C	0.10	Ag	1.00	737	0.10	3.67	This study
		based					
RuPdlr/C	0.20	Ag	1.00	820	0.20	4.10	This study

Table S1. Comparison of AEMFC performance of our catalyst with other reported catalysts



Figure S11. Comparison of a PGM-free, silver-based cathode with the AgPd cathode used in this study, in an MEA with a PdIrRu/C [0.2 mg/cm2 metal loading]. At low current densities where catalytic effects dominate the IV curve, the PGM-free cathode matches the performance of AgPd. At the peak power density of 820 mW/cm² corresponds to 4.1 W/mg_{PGM}.



Figure S12. Galvanostatic experiments carried out at the same conditions as the FC polarization curves, at various current densities for an MEA of 0.2mg anode metal loading. The current densities of 1, 1.4, 1.8 and 2.6 A/cm² have power densities of ca. 600, 755, 860 and 950 mW/cm² respectively.

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