

## Supplementary Information

### An efficient Ag/ionomer interface for hydroxide exchange membrane fuel cells†

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#### 1. Experimental methods

##### 1. Recipes of Ag, Pt, and Ni catalyst inks and preparation of corresponding electrodes

Ag and Pt catalyst inks consist of 100 mg Ag nanoparticles (Quantum Sphere Inc., 30 nm) or 100 mg Pt black (Premetek Co., 5 nm), 25 mg phosphonium ionomer (TPQPOH, 0.5 g of 5wt% TPQPOH solution in 50wt%/50wt% ethanol/water mixture) or 25 mg ammonium ionomer (AS-4, Tokoyama Co., 0.5 g of 5wt% AS-4 solution in n-propanol), 1 g additional deionized water, and 1 g additional ethanol; Ni catalyst ink consists of 500 mg 80% Ni/C nanoparticles (Premetek Co., pre-passivated with 5wt% oxygen atom, 30 nm) and 500 mg TPQPOH ionomer (10 g of the 5wt% TPQPOH solution); The TPQPOH ionomer content of the resulting electrodes is 20wt% for Ag and Pt electrodes, and 50wt% for Ni electrode. After dispersing the catalyst ink by ultra-sonication at 0 °C for one hour, the electrodes were prepared by spraying the sonication-dispersed catalyst ink onto carbon paper (25CC, SGL) to the desired metal loadings: 0.5 mg cm<sup>-2</sup> for Ag or Pt electrode, and 5.0 mg cm<sup>-2</sup> for Ni electrode.

##### 2. In-situ electrochemical surface area (ESA) measurement of Ag and Pt catalysts in HEMFC

With flowing humidified hydrogen through (0.2 L min<sup>-1</sup> of flow rate), Pt anode in the HEMFC serves as the reference electrode (RHE) and the counter electrode simultaneously. At 20 °C, the cyclic voltammogram (CV) was recorded between 0 and 1.5 V vs. RHE (anode) at a scanning rate of 100 mV s<sup>-1</sup> for Ag cathode and the Ag oxidation CV peak at ~1.18 V vs. RHE was used to determine the ESA of Ag using the charge density of 400 μC cm<sup>-2</sup>. The CV was recorded between 0 and 1.1 V vs. RHE at a scanning rate of 50 mV s<sup>-1</sup> for Pt cathode and the Pt-H under-potential deposition region between 0.05 V and ~0.4 V vs. RHE was used to calculate the ESA of Pt using the charge density of 210 μC cm<sup>-2</sup>. During the CV measurement, humidified argon was flowed through the cathode at a flow rate of 0.2 L min<sup>-1</sup>.

##### 3. Preparation of Pt and Ag catalyst coated electrodes for RDE

Pt aqueous suspension (1wt%) and Ag one (2wt%) were prepared by dispersing the Pt black (Premetek Co., 5 nm) and Ag nanoparticles (Quantum Sphere Inc., 30 nm) in deionized water under ultra-sonication. 20 μL of catalyst suspension was deposited on 0.06 μm-alumina-polished glassy carbon electrode (diameter of 5 mm, or effective area of 0.196 cm<sup>2</sup>, Pine Instrument), and then was dried in ambient condition. 10 μL TPQPOH ionomer solution (0.05wt% in 50wt%/50wt% ethanol/water mixture) was then added onto the dried catalyst-coated electrode to secure the catalysts to the disk, and then dried in ambient condition. The resulting loadings of metal catalysts were 100 and 200 μg cm<sup>-2</sup> for Pt and Ag, respectively. The TPQPOH ionomer loading is 250 μg cm<sup>-2</sup> for both cases.

##### 4. Measurement of the ex-situ ESA of Ag and Pt catalysts in RDE

The catalysts' ESAs were measured in a jacketed glass cell (Pine Instruments), which was connected to a temperature-controlled circulating water bath. The catalyst-coated electrode was mounted onto a rotator and immersed into 0.1 M KOH aqueous solution (99.99% metal purity). An Ag/AgCl electrode was employed as the reference electrode and a Pt wire served as the counter electrode. For convenience, all potentials reported in this paper are referenced to the RHE potential. After the electrolyte was saturated with argon, the CV at 20 °C was recorded between 0 and 1.5 V vs. RHE at a scanning rate of 100 mV s<sup>-1</sup> for Ag electrode and between 0 and 1.1 V vs. RHE at a scanning rate of 50 mV s<sup>-1</sup> for Pt electrode. The CV peak at ~1.18 V vs. RHE was used to determine the

ESA of Ag using the charge density of  $400 \mu\text{C cm}^{-2}$ , and the Pt-H under-potential deposition region between 0.05 V and  $\sim 0.4$  V vs. RHE was used to calculate the ESA of Pt using the charge density of  $210 \mu\text{C cm}^{-2}$ .

### 5. Oxygen reduction reaction (ORR) activity measurement of Ag and Pt in RDE

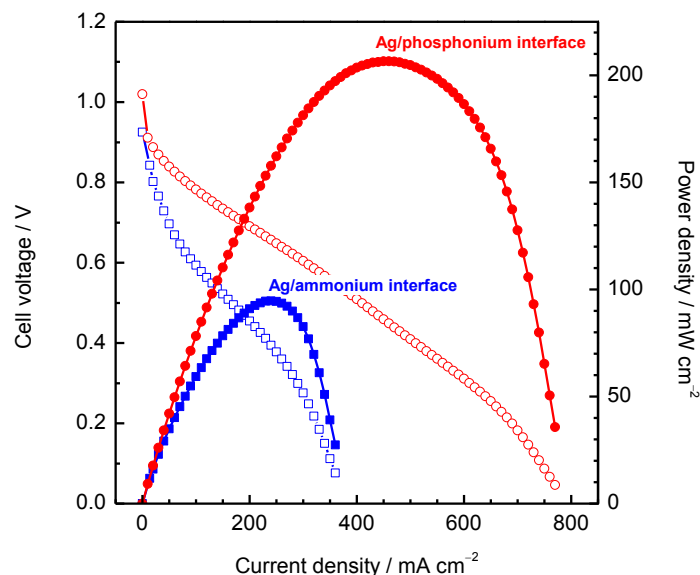
ORR activities of Ag and Pt black catalysts were measured in the abovementioned jacketed glass cell filled with 0.1 M KOH as supporting electrolyte. After the electrolyte was purged with pure oxygen, polarization curves were recorded between  $\sim 0.03$  V and 1.13 V vs. RHE at a scanning rate of  $10 \text{ mV s}^{-1}$  and a rotating rate of 1600 rpm at 10, 20, 30, and 40 °C, respectively. To minimize the possible contamination due to glass alkaline corrosion, freshly prepared 0.1 M KOH was used for ORR measurement at each temperature. The cell resistance was measured immediately after ORR measurements at each temperature, and the real part of the impedance at 1 kHz was taken as the cell internal resistance from the AC impedance spectrum (frequency from 32 kHz to 100 Hz and voltage perturbation of 10 mV). Based on the internal resistance (IR)-corrected ORR polarization curves, the kinetic current,  $i_k$ , at 0.85 V vs. RHE was obtained using the Koutecky-Levich equation.

### 6. Fabrication of membrane electrode assembly (MEA) and fuel cell test

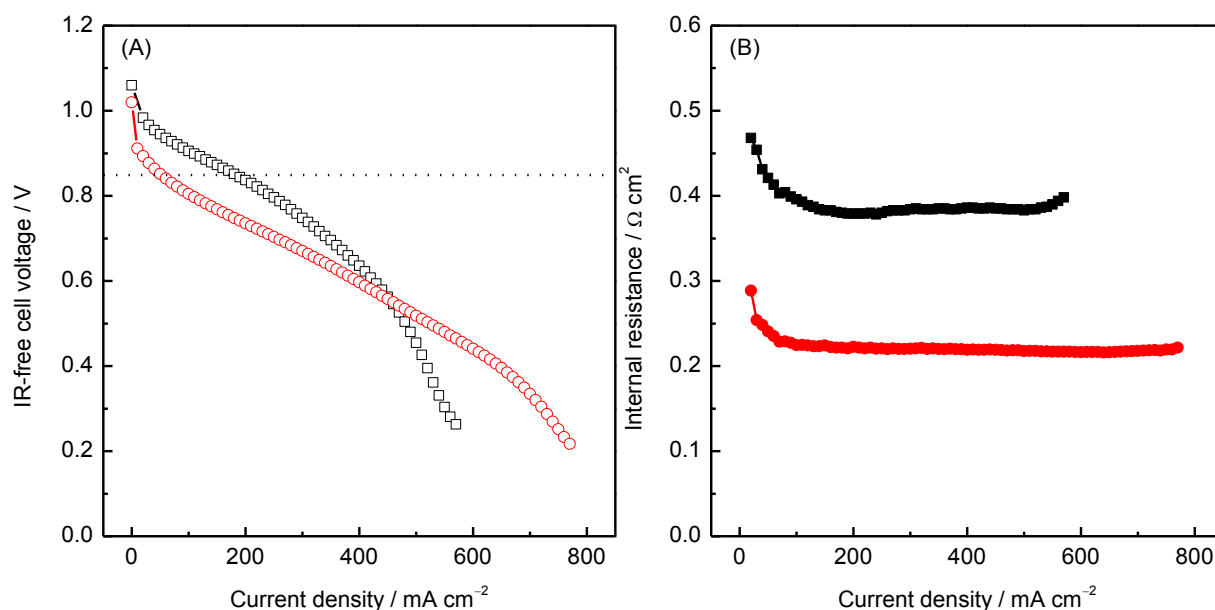
The membrane electrode assemblies (MEAs) with  $5 \text{ cm}^2$  active area were prepared by pressing an anode, a piece of HEM, and an cathode under  $120 \text{ kgf cm}^{-2}$  for 5 min. The pressing temperature used was 20 °C and 60 °C for TPQPOH152 membrane and FAA membrane, respectively. The MEA was assembled in a single cell fixture for the HEMFC test. Prior to data collection, the fuel cells were activated by discharging at constant current density from zero to maximum current density with the increment step of  $20 \text{ mA cm}^{-2}$  every 5 min for all Pt electrodes-based MEA or Pt anode and Ag cathode-based MEA. The fuel cell with Ni anode and Ag cathode-based MEA was activated by discharging at constant current density from zero to maximum current density with the increment step of  $2 \text{ mA cm}^{-2}$  every 5 min. The I-V polarization curves were obtained under the operation conditions: pure  $\text{H}_2$  and  $\text{O}_2$  as fuel and oxidant with  $0.2 \text{ L min}^{-1}$  flow rate and 250 kPa back pressure, 70 °C and 80 °C at anode and cathode humidifiers, respectively, and 70 or 80 °C as the cell temperature.

Detailed synthesis and preparation procedures of the TPQPOH ionomer<sup>2</sup> and membrane<sup>3</sup> were described in our previous work.

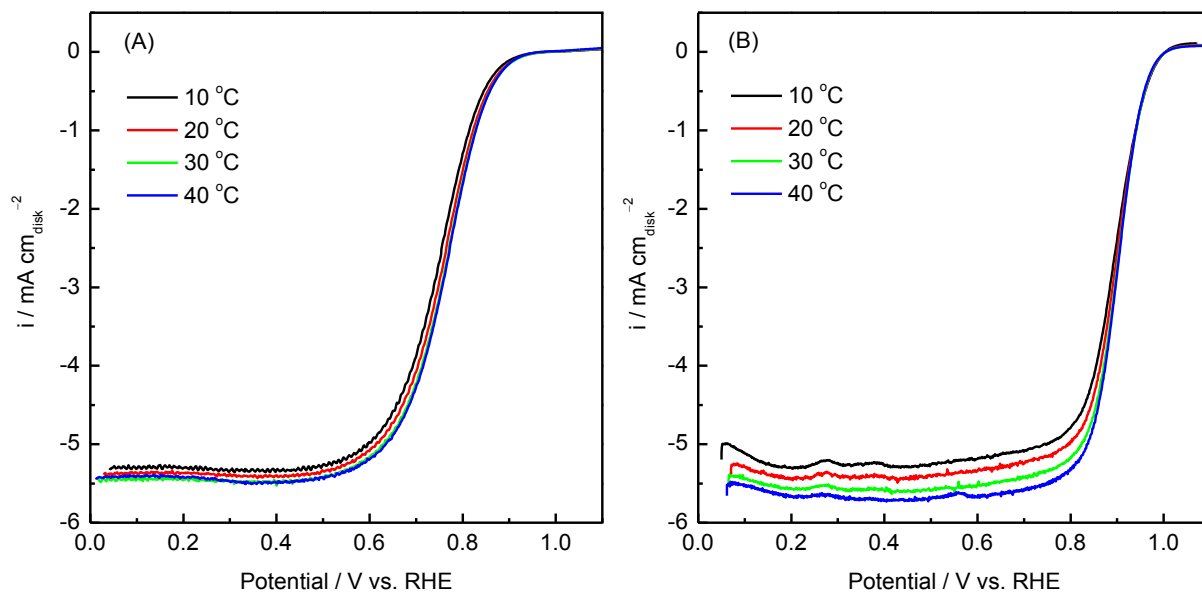
## 2. Figures



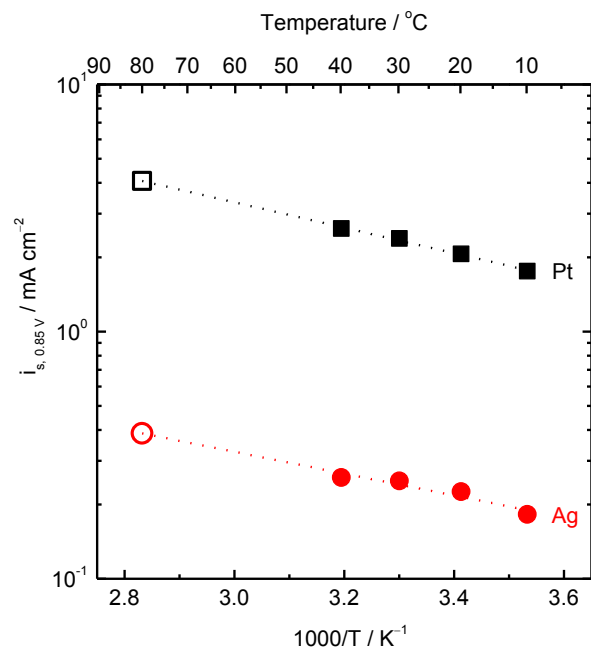
**Fig. S1** Polarization curves (open symbols) and power density curves (solid symbols) of Ag/phosphonium ionomer interface (○, ●) and Ag/ammonium ionomer interface (□, ■) based HEMFCs. Anode for both cases: Pt black (Premetek Co., 5 nm), Pt loading of  $0.5 \text{ mg cm}^{-2}$ , and TPQPOH ionomer with 20wt% content. Cathode: Ag catalyst (Ag nanoparticle, Quantum Sphere Inc., 30 nm) and Ag loading of  $0.5 \text{ mg cm}^{-2}$  for both Ag/phosphonium ionomer interface (TPQPOH phosphonium ionomer and 20% ionomer content) and Ag/ammonium ionomer interface (AS-4 ammonium ionomer, Tokoyama Co., and 20% ionomer content). HEM: FAA commercial membrane (Fuma-Tech, 70  $\mu\text{m}$  thickness, and  $17 \text{ mS cm}^{-1}$  hydroxide conductivity at 20 °C). Test conditions: the cell temperature of 80 °C, humidifier temperatures of 70 °C and 80 °C for  $\text{H}_2$  and  $\text{O}_2$ , respectively, a flow rate of  $0.2 \text{ L min}^{-1}$  and a back pressure of 250 kPa for both  $\text{H}_2$  and  $\text{O}_2$ .



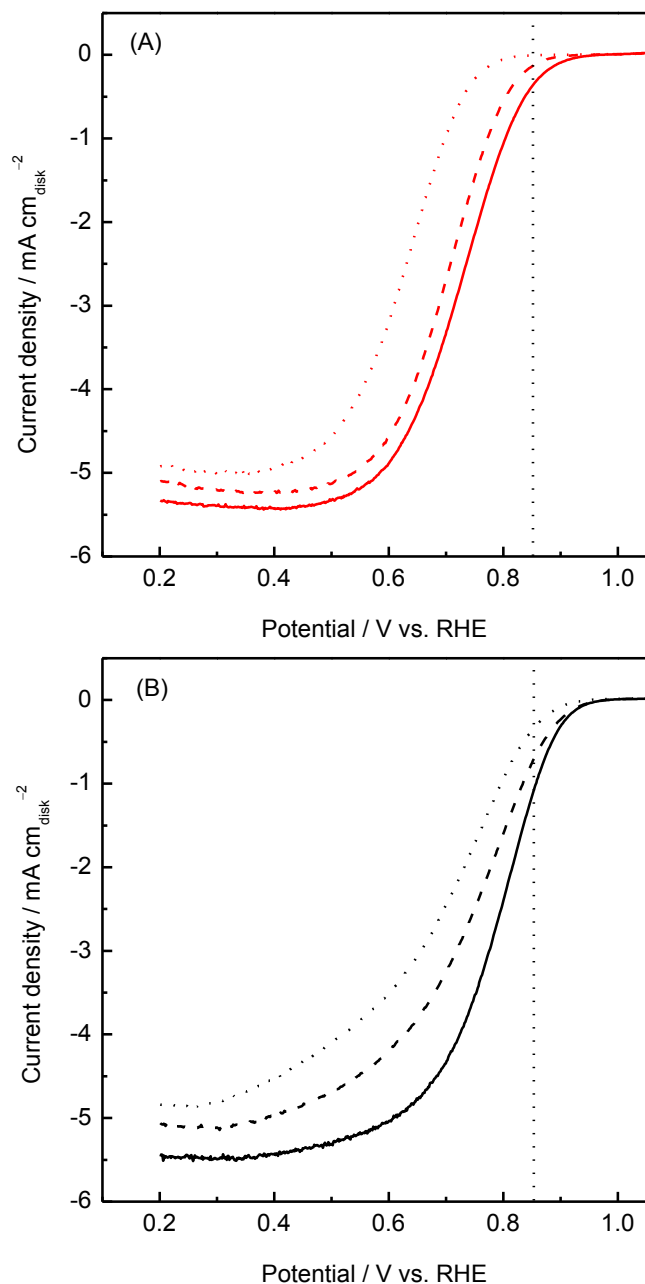
**Fig. S2** (A) Internal resistance (IR)-free cell voltage curves of Ag/phosphonium cathode interface (red open circles, ○) and Pt/phosphonium cathode interface (black open squares, □) incorporated HEMFCs. (B) Internal resistance curves of Ag/phosphonium cathode interface (red solid circles, ●) and Pt/phosphonium cathode interface (black solid squares, ■) incorporated HEMFCs. Pt anode for both cases: Pt black (Premetek Co., 5 nm), Pt loading of 0.5 mg cm<sup>-2</sup>, and TPQPOH ionomer with 20wt% content; Metal loading of 0.5 mg cm<sup>-2</sup> and TPQPOH ionomer with 20wt% content for both Pt cathode (Pt black, Premetek Co., 5 nm) and Ag cathode (Ag nanoparticle, Quantum Sphere Inc., 30 nm); HEM: FAA commercial membrane (Fuma-Tech, 70 μm thick, 17 mS cm<sup>-1</sup> hydroxide conductivity at 20 °C); Test conditions: cell temperature of 70 °C, humidifier temperatures of 70 °C and 80 °C for H<sub>2</sub> and O<sub>2</sub>, respectively, flow rate of 0.2 L min<sup>-1</sup> and back pressure of 250 kPa for both H<sub>2</sub> and O<sub>2</sub>.



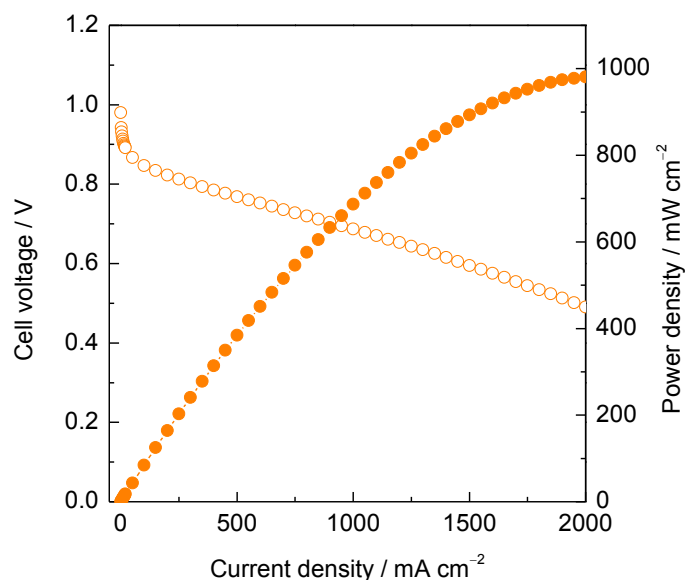
**Fig. S3** (A) RDE ORR polarization curves on Ag (Ag nanoparticle, Quantum Sphere Inc., 30 nm) at 10, 20, 30, and 40 °C; (B) RDE ORR polarization curves on Pt (Pt black, Premetek Co., 5 nm) at 10, 20, 30, and 40 °C. Test conditions: disk electrode area of 0.196 cm<sup>2</sup>, metal loading of 200 and 100 μg cm<sup>-2</sup> for Ag and Pt, respectively, TPQPOH ionomer loading of 250 μg cm<sup>-2</sup> for both Ag and Pt, O<sub>2</sub>-saturated 0.1 M KOH as supporting electrolyte, scanning rate of 10 mV s<sup>-1</sup>, and rotating speed of 1,600 rpm.



**Fig. S4** *Ex-situ* RDE ORR specific activities on Ag nanoparticle (Quantum Sphere Inc., 30 nm, red circles) and Pt black (Premetek Co., 5 nm, black squares) at 0.85 V vs. RHE measured at 10–40 °C (solid symbols) and extrapolated to 80 °C (open symbols). Test conditions: disk electrode area of 0.196 cm<sup>2</sup>; metal loading of 200 and 100 μg cm<sup>-2</sup> for Ag and Pt, respectively; TPQPH ionomer loading of 250 μg cm<sup>-2</sup> for both Ag and Pt, O<sub>2</sub>-saturated 0.1 M KOH as supporting electrolyte, potential scanning rate of 10 mV s<sup>-1</sup>, and rotating speed of 1600 rpm.

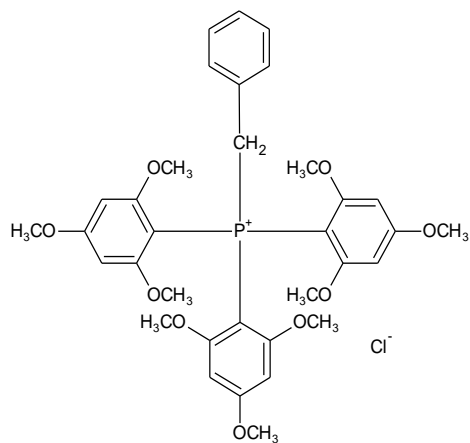


**Fig. S5** (A) RDE ORR polarization curves on Ag bulk disk electrode (red lines); (B) RDE ORR polarization curves on Pt bulk disk electrode (black lines). O<sub>2</sub>-saturated supporting electrolytes: 0.1 M KOH (solid lines), 1 mM BTQPCI-containing 0.1 M KOH (dash lines), and 10 mM BTQPCI-containing 0.1 M KOH (dot lines). Test conditions: cell temperature of 20 °C, potential scanning rate of 10 mV s<sup>-1</sup>, disk electrode area of 0.196 cm<sup>2</sup>, and rotating speed of 1600 rpm.



**Fig. S6** Polarization curve (open symbols) and power density curve (solid symbols) of an H<sub>2</sub>/O<sub>2</sub> PEMFC. Pt electrode for both anode and cathode: carbon supported Pt (Premetek Co., 20% Pt/C), Pt loading of 0.2 mg cm<sup>-2</sup>, and Nafion ionomer with 35wt% content (or loading of 0.54 mg cm<sup>-2</sup>) for both anode and cathode; PEM: 50 μm Nafion212 membrane; Test conditions: cell temperature of 70 °C, humidifier temperature of 70 °C, flow rate of 0.2 L min<sup>-1</sup> and back pressure of 250 kPa for both H<sub>2</sub> and O<sub>2</sub>.

### 3. Scheme



**Scheme S1** Chemical structure of benzyl tris(2,4,6-trimethoxyphenyl) quaternary phosphonium chloride (BTQPCI). BTQPCI was synthesized by reacting benzyl chloride and tris(2,4,6-trimethoxyphenyl)phosphine in tetrahydrofuran at 40 °C for 2 hours.

## 4. Table

**Table S1** Comparison of Ni, Ag based HEMFC and Pt based PEMFC (under the same test conditions: 70 °C cell temperature and 250 kPa back pressure).

Fuel cell	Catalyst (metal loading / mg cm <sup>-2</sup> ) and membrane			Performance			Cost			P <sub>c</sub> <sup>e</sup> / W US\$ <sup>-1</sup>
	Anode catalyst	Cathode catalyst	Membrane	OCV <sup>a</sup> / V	IR <sup>b</sup> / Ωcm <sup>2</sup>	PD <sub>0.7 V</sub> <sup>c</sup> / mW cm <sup>-2</sup>	Anode-metal <sup>d</sup> / US\$ g <sup>-1</sup>	Cathode-metal <sup>d</sup> / US\$ g <sup>-1</sup>	Membrane / US\$ dm <sup>-2</sup>	
HEMFC	80% Ni/C (5.0)	Ag (0.5)	TPQPOH152	1.06	0.145	75	0.024	0.64	0.02	117
PEMFC	20% Pt/C (0.2)	20% Pt/C (0.2)	Nafion212	0.98	0.078	660	48.2	48.2	6.64	7.7

<sup>a</sup> OCV, open circuit voltage. <sup>b</sup> IR, internal resistance. <sup>c</sup> PD<sub>0.7 V</sub>, power density at 0.7 V cell voltage. <sup>d</sup> Based on a 5-year average price from June 2006 to June 2011 from [www.metalprices.com](http://www.metalprices.com). <sup>e</sup> P<sub>c</sub>, cost-normalized power (0.7 V cell voltage), which is solely based on the cost of pure metals and membrane although other fuel cell components may have contributions. <sup>f</sup> Collected from [www.nafionstore.com](http://www.nafionstore.com) in June 2011.

## References

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2. S. Gu, R. Cai, T. Luo, Z. W. Chen, M. W. Sun, Y. Liu, G. H. He and Y. S. Yan, *Angew Chem Int Edit*, 2009, **48**, 6499-6502.
3. S. Gu, R. Cai, T. Luo, K. Jensen, C. Contreras and Y. S. Yan, *Chemsuschem*, 2010, **3**, 555-558.