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Supporting Information

High-Performance Supportless Silver Nanowire Catalyst for Anion

Exchange Membrane Fuel Cells

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1 1. Estimation of the porosity of anode and cathode

2 For the anode, the density of carbon (ρ_C) is about 1.80 g cm⁻³. The porous Vulcan XC-3 72 carbon has a total pore volume (V_{pore}) of 0.32 cm³ g⁻¹. The density of porous 4 carbon particle, ρ_{Cp} is

5
$$\rho_{Cp} = \frac{1}{\frac{1}{\rho_c} + V_{pore}} = \frac{1}{\frac{1}{1.80} + 0.32} = 1.14 \text{ g cm}^{-3}$$

6 The density of 60 wt.% Pt/C, $\rho_{Pt(60\%)/C}$ is

7
$$\rho_{Pt(60\%)/C} = \frac{1}{\frac{x_{Pt}}{\rho_{Pt}} + \frac{x_{Cp}}{\rho_{Cp}}} = \frac{1}{\frac{0.6}{21.46} + \frac{0.4}{1.14}} = 2.64 \ g \ cm^{-3}$$

8 In the anode, the active surface area and thickness are 5 cm² and 7.7×10^{-4} cm, 9 respectively. Hence, the volume occupied by Pt/C, $V_{Pt(60\%)/C}$ is

10
$$V_{Pt(60\%)/C} = \frac{Active Area \times \frac{Pt \ loading}{0.6}}{\rho_{Pt(60\%)/C}} = \frac{5 \times \frac{0.4 \times 10^{-3}}{0.6}}{2.64} = 1.26 \times 10^{-3} \ cm^{3}$$

11 The density of home-made ionomer determined by experiment is 0.94 g cm⁻³.
12 Therefore, the volume occupied by ionomer, V_{ionomer} is

13
$$V_{ionomer} = \frac{Active Area \times \frac{ionomer}{Pt/C} \times \frac{Pt \ loading}{0.6}}{\rho_{ionomer}} = \frac{5 \times \frac{20}{80} \times \frac{0.4 \times 10^{-3}}{0.6}}{0.94} = 0.89 \times 10^{-3} \ cm^{3}$$

14 The volume of the anode, V_{anode} is

$$V_{anode} = Active Area \times Thickness = 5 \times 7.7 \times 10^{-4} = 3.85 \times 10^{-3} cm^3$$

16 Therefore, the porosity of anode is

17
$$\varepsilon_{anode} = \frac{V_{anode} - V_{Pt(60\%)/C} - V_{ionomer}}{V_{anode}} \times 100\% = \frac{3.85 - 1.26 - 0.89}{3.85} \times 100\% = 44.16\%$$

For the cathode, the density of silver is 10.49 g cm⁻³. If the loading of Ag NWs in the cathode is 1.05 mg cm⁻², hence the volume occupied by Ag NWs, V_{Ag} is

20
$$V_{Ag} = \frac{Active \ Area \times Ag \ loading}{\rho_{Ag}} = \frac{5 \times 1.05 \times 10^{-3}}{10.49} = 1.26 \times 10^{-3} \ cm^3$$

21 Also, the volume occupied by ionomer, $V_{ionomer}$ is

22
$$V_{ionomer} = \frac{Active Area \times \frac{ionomer}{Ag} \times Ag \ loading}{\rho_{ionomer}} = \frac{5 \times \frac{20}{80} \times 1.05 \times 10^{-3}}{0.94} = 1.40 \times 10^{-3} \ cm^{3}$$

23 The volume of the cathode, V_{cathode} is

24
$$V_{cathode} = Active Area \times Thickness = 5 \times 4.2 \times 10^{-4} = 2.10 \times 10^{-3} cm^3$$

25 Therefore, the porosity of **cathode** is

26
$$\varepsilon_{cathode} = \frac{V_{cathode} - V_{Ag} - V_{ionomer}}{V_{cathode}} \times 100\% = \frac{2.10 - 0.50 - 1.40}{2.10} \times 100\% = 9.52\%$$

27

28

2. Supplementary Figures



Figure S1. Low-resolution SEM image of as-prepared Ag NWs.



Figure S2. The dependence of electron transfer number on the potential for Ag NWs. The inset shows Tafel plot for Ag NWs.



Figure S3. (a) A typical low-revolution TEM image of home-made Ag nanoparticles (NPs) supported on graphene nanosheets (Ag/GNS); (b) high-revolution TEM image of Ag NPs. The interfringe distanced was measured to be 2.30Å, which could be indexed to the (111) plane of the *fcc*-structured Ag.



Figure S4. Polarization curves (filled symbols) and power density curves (empty symbols) of H₂/O₂ AEMFCs with Ag NWs, Ag NWs physically mixed with 20 wt.% GNS, Ag/GNS and commercial Pt/C as the cathode catalyst. The Ag loading in the Ag-based catalyst was 1.05 mg_{Ag} cm⁻² while the Pt loading in commercial Pt/C catalyst was 0.5 mg_{Pt} cm⁻². The ionomer loading in all the samples was controlled at 20 wt.%. Other operating parameters were stated in the experimental section.



Figure S5. CV curves of Pb UPD in Ag/GNS. The electrochemical surface area (ECSA) was 10.65 m² g⁻¹ through analyzing the charge associated with Pb underpotential deposition (UPD) on Ag nanoparticles.



Figure S6. AC impedance spectra of AEMFCs before and after constant current discharge (Frequency: 100 kHz-0.1 Hz; temperature: 60°C; Anode: hydrated hydrogen gas, 500 sccm; cathode: hydrated oxygen gas, 500 sccm).