

Robust and reliable oxygen reduction activity of porous Pt-Cu core-shell catalysts

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Introduction

Polymer electrolyte fuel cells (PEMFCs) are energy conversion devices that catalyze the conversion of molecular hydrogen and oxygen to water. They have quite high conversion efficiencies compared to conventional technologies based on heat engines. However, PEMFC performance is limited by the cathodic catalytic reaction where oxygen is reduced to water (ORR).

Here, we utilize galvanic displacement to synthesize highly active, tunable PtCu ORR catalysts that have specific activities exceeding $1200 \mu\text{A}/\text{cm}^2$ of active Pt at 0.9 V (298 K). Electron microscopy and BET surface analysis indicate our catalyst has extremely high porosity ($> 10 \text{ m}^2/\text{g}$), which acts to maximize mass transport and increase active surface area.

Experimental

A nanoporous Cu support was formed by etching Al from an in-house prepared CuAl alloy, with composition ranging between 20 to 50 wt% Cu. Upon etching, the nanoporous support (Figure 1) provides a high surface area of 10-15 m^2/g . Pt was deposited onto the support via a galvanic displacement reaction at a constant rotation rate to ensure mass transfer control for 0.5 to 60 min, resulting in Pt:Cu ratios ranging from 0.5 to 2.1.

ORR activity was evaluated using a rotating ring disc electrode (PINE Instruments) as working electrodes, and Pt and a reversible hydrogen electrode as the counter and reference electrode, respectively. All experiments are performed in 0.1 M HClO_4 and 0.1 M H_2SO_4 at room temperature.

Results and Discussion

The open circuit potential (OCP) during the galvanic displacement process (298K, 150 RPM) shows an appreciable change within the first 5 minutes of deposition (Figure 1), followed by a plateau after 5 minutes. This is an indicator that surface structure is not dramatically changing after 5 minutes, but may be significantly tuned within the first 4 minutes.

After normalizing catalyst activities to the electrochemical surface area (ESA) from the H_{upd} peaks of Pt, the resulting specific activities at 0.9 V are shown in Figure 2. The 3 min 50 °C PtCu catalyst has an activity 72% higher than the current state-of-the-art Pt catalyst (Pt/C). Furthermore, the specific activities of all our galvanically displaced catalysts exceed the 2017 DOE target for platinum group metal specific activity ($720 \mu\text{A}/\text{cm} @ 0.9 \text{ V}; 80 \text{ }^\circ\text{C}$). Generally, the specific activity seems to decrease as deposition time increases. This trend may be explained by considering that shorter Pt deposition times should normally translate to a thinner Pt overlayer. Observed ORR enhancement may be due to lattice strain effects.¹⁻²

Mass activities @ 0.9 V were also obtained using a Perkin-Elmer Elan 6000 inductively coupled plasma mass spectrometer (ICP-MS) after electrochemical measurements were taken and electrodes stripped of

catalysts with aqua regia. The mass activity of our 3 min 50 °C PtCu catalyst is 0.25 A/mg Pt, which is ~40% higher than Pt/C (0.18 A/mg Pt).

Our optimized catalysts also exhibit good stability (Figure 3). Stability tests were performed by cycling the potential 10,000 times between 0.6-1.1 V in oxygenated 0.1 M HClO_4 for 10,000 cycles (50 mV/s). There was a 20% decrease in electrochemical surface area (ESA) during the first 7000 cycles, after which the activity approaches a steady value. Interestingly, the raw ORR currents obtained for cycle 1 and cycle 10,000 were the same, indicating that the specific activity of the catalyst increased over the 10,000 cycles. We are confident that we will be able to address the ESA loss and improve mass activity through fine tuning the galvanic displacement process. At present, we are in the process of conducting a systematic study to better understand the catalytic enhancement offered by our catalysts.

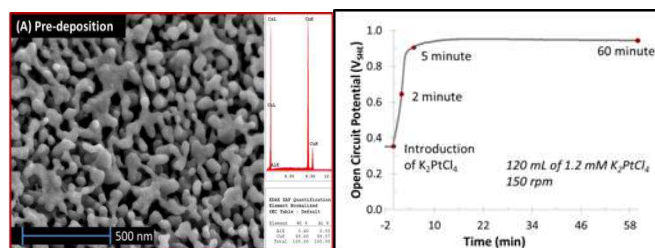


Figure 1. (left) SEM micrographs/ EDS spectra for the nanoporous Cu support prior to galvanic displacement. (right) open circuit potential as a function of galvanic displacement reaction time.

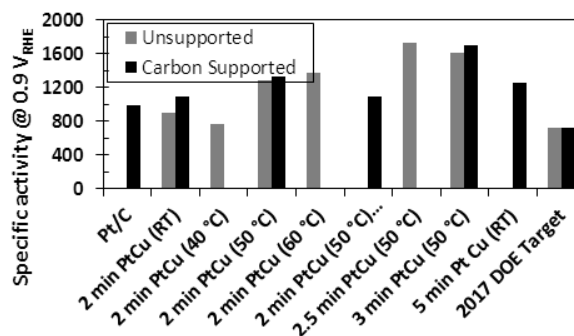


Figure 2. ORR specific activity for PtCu catalysts compared to Pt/C at 0.9 V vs. RHE. Electrochemical measurements performed with RDE in 0.1 M HClO_4 at 298 K.

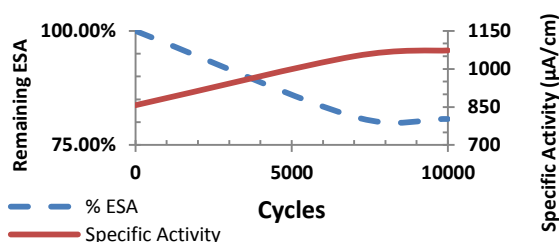


Figure 3. Stability of 3 min 50 °C PtCu catalyst based on Pt-ESA and specific activity losses over 10,000 cycles.

References

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