



Cathode catalyst degradation in PEM fuel cells – a differential electrochemical mass spectrometry study

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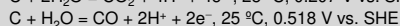
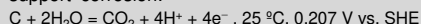
Introduction

Background: Cathode electrocatalyst durability (nanoparticle Pt on carbon black support) is one of the key barriers for PEMFC commercialization.

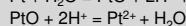
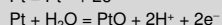
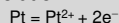
Two main reasons:

1. Carbon support corrosion

Two main proposed pathways for the carbon support corrosion:



2. Pt dissolution



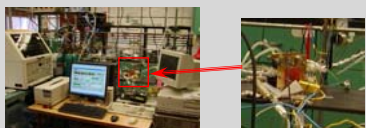
Pt oxidation is a pivotal step of the Pt dissolution.

Objective: Study the carbon support corrosion and Pt oxidation/reduction with DEMS spectra.

Experiment

Differential electrochemical mass spectrometry (DEMS):

An on-line mass spectrometer samples gases from the cathode of a 5 cm² single PEMFC, with potential cycling imposed by an electrochemical potentiostat. Humidified H₂ and He gases were fed to anode and cathode, respectively.



5 cm² single PEMFC

Results and discussion

1. Locate the potential to construct DEMS

CO₂, H₂ and O₂ exiting from the cathode during potential cycling (Figure 1: a) were detected by the MS. The mass spectra (Figure 1: b) were turned into the DEMS spectra (Figure 1: c, d) by identifying the potentials using the CO₂ mass signals at 1400 mV as references.

2. Identify which components, Pt or C, cause H₂ and CO₂ signal changes (Figure 2)

- H₂ signal changes are related to the Pt existing in Pt and Pt/C cathodes. The same shape means same mechanisms.
- CO₂ comes from carbon support.
- Pt catalyzes the CO₂ production.
- Three peaks in the middle represent three different kinds of reactions.
- Pt/C cathode has stronger CO₂ signal at 1400 mV than C cathode.

Results and discussion

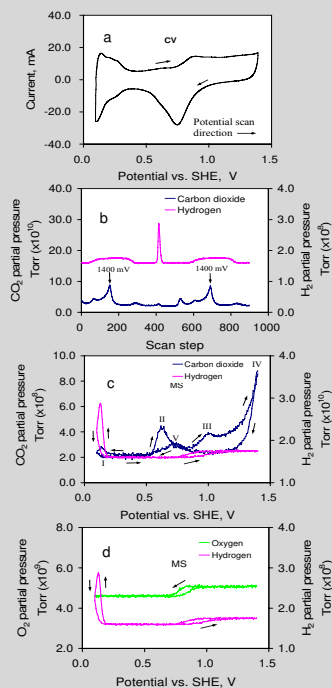


Fig. 1: Pt/C cathode DEMS spectra: (a) CV; (b) locate the potentials; (c) DEMS spectra of H₂ and CO₂; and (d) DEMS spectra of H₂ and O₂

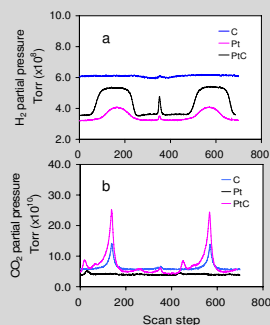


Fig. 2: MS spectra for C, Pt and Pt/C cathodes: (a) H₂ MS spectra and (b) CO₂ MS spectra

Results and discussion

3. DEMS spectra interpretation

3.1 CO₂ signal (Figure 1: c)

- Maximum I at 100 mV: C reacts with hydrogen peroxide.
- Maximum II (peak II) at 600 mV: CO_{surf} oxidized to CO₂.
- Maximum III (peak III) at 900 mV: carbon surface oxides groups oxidized to CO₂.
- Maximum IV (peak IV) at 1400 mV: C directly oxidized to CO₂.
- Maximum V at 750 mV (cathodic scan): removal of [O] or [OH] from Pt and transfer to carbon surface to help to produce CO₂.

3.2 H₂ signal

- Peak at 100 mV: hydrogen desorption from H_{OPD} (Figure 1: c and Figure 3)

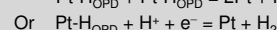
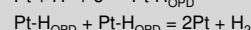
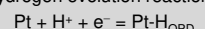
Two kinds of H in 100 – 400 mV

- Underpotential deposition H, H_{UPD} (main part)
- Overpotential deposition H, H_{OPD} (small part)

Mechanism

- Only H_{OPD} contributes to this peak

- Hydrogen evolution reaction (HER)



- The size of H₂ peak is very small compared to the electrochemical surface area from CV.
- HER has positive temperature effect

- H₂ Plateau: (Figure 1: c and Figure 3)

- Starts around 0.9 V (anodic scan), where the Pt begins to be oxidized; ends around 0.8 V (cathodic scan), where the PtOx reduction ends. This matches that in CV. One advantage of DEMS is that it can resolve the currents of Pt oxidation and C oxidation, which cannot in CV.
- PtOx has low hydrogen oxidation catalytic effect so as to increase the hydrogen signal.

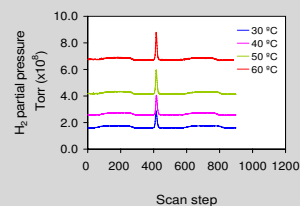


Fig. 3: Hydrogen MS spectra peaks

Results and discussion

3.3 O₂ signal: Plateau (Figure 1: d)

PtOx has lower oxygen (leaking from air) reduction catalytic effect than Pt which results the oxygen signal increase.

4. Temperature dependence of carbon corrosion (Figure 4)

- CO₂ signal increase with temperature, which means higher degradation, though better performance at higher temperature.
- Arrhenius plot for CO₂ concentration at 1400 mV shows very good linear, and positive temperature dependence.

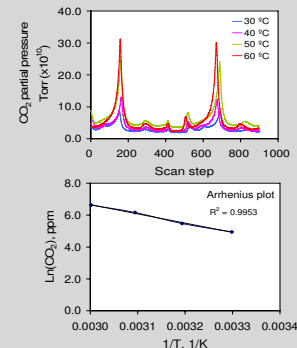


Fig. 4: Temperature effects on carbon corrosion

Summary and future work

- DEMS is a powerful tool to investigate the carbon support corrosion, Pt oxidation/reduction and their interplay during electrocatalyst degradation in the cathode of PEMFC, by correlating the products and probe gases changes to specific potentials.
- More spectroscopy methods in situ are being considered to complement the DEMS, such as Raman, IR and X-ray absorption fine structure at synchrotron.

Acknowledgements

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