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:

$C + 2H_2O = CO_2 + 4H^+ + 4e^-$, 25 ºC, 0.207 V vs. SHE

$C + H_2O = CO + 2H^+ + 2e^-$, 25 ºC, 0.518 V vs. SHE

2. Pt dissolution

$Pt = Pt^{2+} + 2e^-$

$Pt + H_2O = PtO + 2H^+ + 2e^-$

$PtO + 2H^+ = Pt^{2+} + H_2O$

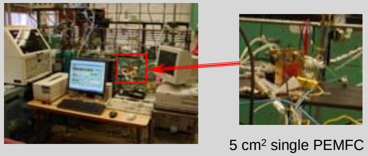
Pt oxidation is a pivotal step of the Pt dissolution.

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 H_2 and He gases were fed to anode and cathode, respectively.



5 cm² single PEMFC

Results and discussion

1. Locate the potential to construct DEMS

CO_2, H_2 and O_2 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 indentifying the potentials using the CO_2 mass signals at 1400 mV as references.

2. Identify which components, Pt or C, cause H_2 and CO_2 signal changes (Figure 2)

- H_2 signal changes are related to the Pt existing in Pt and Pt/C cathodes. The same shape means same mechanisms.
- CO_2 comes from carbon support.
- Pt catalyzes the CO_2 production.
- Three peaks in the middle represent three different kinds of reactions.
- Pt/C cathode has stronger CO_2 signal at 1400 mV than C cathode.

Results and discussion

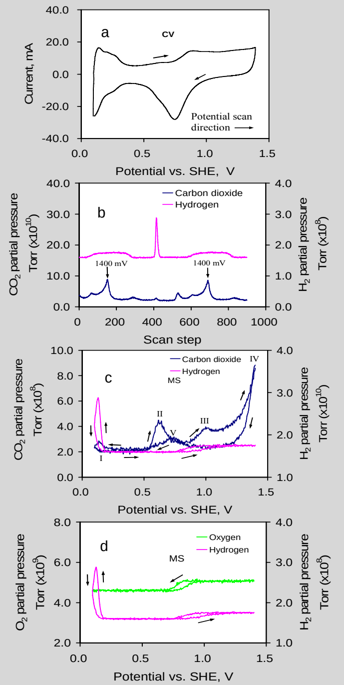


Fig. 1: Pt/C cathode DEMS spectra: (a) CV; (b) locate the potentials; (c) DEMS spectra of H_2 and CO_2; and (d) DEMS spectra of H_2 and O_2

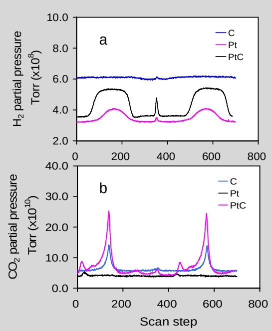


Fig. 2: MS spectra for C, Pt and Pt/C cathodes: (a) H_2 MS spectra and (b) CO_2 MS spectra

Results and discussion

3. DEMS spectra interpretation

3.1 CO_2 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 CO_2.
- Maximum III (peak III) at 900 mV: carbon surface oxides groups oxidized to CO_2.
- Maximum IV (peak IV) at 1400 mV: C directly oxidized to CO_2.
- Maximum V at 750 mV (cathodic scan): removal of [O] or [OH] from Pt and transfer to carbon surface to help to produce CO_2 .

3.2 H_2 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)

    $Pt + H^+ + e^- = Pt\text{-}H_{OPD}$

    $Pt\text{-}H_{OPD} + Pt\text{-}H_{OPD} = 2Pt + H_2$

    Or $Pt\text{-}H_{OPD} + H^+ + e^- = Pt + H_2$
  - The size of H_2 peak is very small compared to the electrochemical surface area from CV.
  - HER has positive temperature effect

- H_2 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.

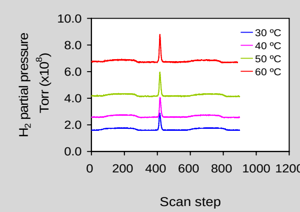


Fig. 3: Hydrogen MS spectra peaks

Results and discussion

3.3 O_2 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)

- CO_2 signal increase with temperature, which means higher degradation, though better performance at higher temperature.
- Arrhenius plot for CO_2 concentration at 1400 mV shows very good linear, and positive temperature dependence.

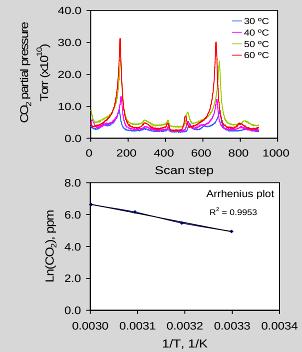


Fig. 4: Temperature effects on carbon corrosion

Summary and future work

1. 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.
2. 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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