

Impact of CeO_x additives on cathode catalyst layer poisoning

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During normal operation of proton exchange membrane fuel cells (PEMFCs), free radicals (OH[•], OOH[•], H[•]) are formed which attack the membrane leading to significant performance loss, and eventual membrane failure due to pinhole and/or crack formation^{1,2}. In an effort to reduce this commonly observed mode of membrane degradation, the addition of free radical scavengers into the anode catalyst layer (ACL), cathode catalyst layer (CCL), and/or the membrane has been investigated³. These free radical scavengers are typically salts (such as Mn²⁺ or Ce³⁺)³, or oxides such as CeO₂². Through OCV accelerated stress testing (designed to stress the membrane), it has been demonstrated that these additives can greatly increase membrane lifetime by consuming free radicals before they are able to attack the membrane³.

While these antioxidants greatly improve membrane lifetime, they have a deleterious impact on performance, particularly when the cathode is degraded⁴. Specifically, the antioxidant cations (released as Ce³⁺/Ce⁴⁺ through dissolution in the case of CeO_x) will accumulate in the cathode catalyst layer through strong interactions with the sulfonate in the ionomer. These cations then compete with protons for sulfonate sites in the CCL, leading to increased CCL ionic resistance and a subsequent loss in performance. This effect is more evident once the cathode has degraded as the reaction distribution shifts towards the cathode-GDL interface. Controlling the rate of CeO_x dissolution is therefore of great importance, as it may be possible to maintain sufficient Ce cations for free radical scavenging, while minimizing the impact of these cations on the CCL. Therefore, this presentation focuses on the impact of CeO_x crystallite size on dissolution rate. Three different CeO_x samples were synthesized, and characterized using XRD and gas sorption (Table 1).

Table 1 Physical properties of the three CeO_x samples, and one commercial CeO_x sample.

Sample*	Crystallite Size (111)	BET Surface Area (m ² /g)
Commercial	30 nm	55
CeO _x 800 °C	25 nm	9
CeO _x 600 °C	13 nm	30
CeO _x 200 °C	6 nm	98

* The temperature refers to the calcination temperature used during the synthesis of the particles.

The chemical stabilities of these CeO_x samples were investigated in 1 M H₂SO₄ using UV-visible spectroscopy to monitor the concentration of Ce³⁺/Ce⁴⁺ cations. The trend in chemical stability was found to be: CeO_x 800 °C > CeO_x 600 °C > Commercial > CeO_x 200 °C (Fig. 1a and Fig. 1b).

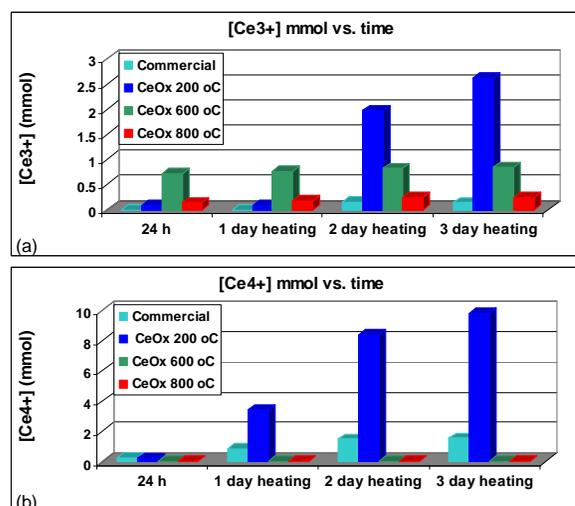


Figure 1 Concentration vs. time for (a) Ce³⁺ and (b) Ce⁴⁺ cations as a result of CeO_x dissolution in 1 M H₂SO₄.

In-situ testing was then performed by incorporating the CeO_x additives into the anode catalyst layer of a membrane electrode assembly (MEA). Accelerated stress testing (AST) was then performed on each MEA (1.3 V upper potential limit, 0.6 V lower potential limit for 4700 cycles) to evaluate the impact of the CeO_x additives on end of life (EOL) performance. Significantly, despite the clear differences in chemical stability found through ex-situ testing, no difference in EOL performance was observed among the MEAs prepared using the four different CeO_x additives. This may suggest that at the loadings used for this study, the CCL becomes saturated with Ce cations even with the most stable CeO_x, prepared at 800 °C.

Finally, the impact of relative humidity (RH) was also investigated. By varying the anode RH between 50 and 100 %, it was determined that anode RH has a large impact on EOL performance of the MEAs containing CeO_x. The effect is believed to be related to the dissolution rate of CeO_x,

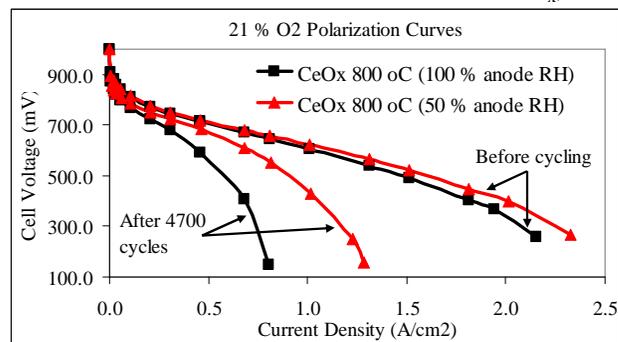


Figure 2 Polarization curves obtained before and after cycling to 4700 cycles under 100 % anode RH (squares) or 50 % anode RH (triangles).

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