

Structurally tuned nitrogen doped cerium oxide as a superior free radical scavenger for mitigating polymer electrolyte membrane degradation

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Introduction:

The chemical degradation processes that occur in a hydrogen/air polymer electrolyte membrane (PEM) fuel cell are attributed to reactive oxygen species (ROS) that are generated in-situ through both chemical and electrochemical pathways during fuel cell operation.^{1,2} Hydrogen peroxide (H_2O_2) is an intermediate formed in both pathways and is known to form free radical ROS in the presence of transition metal ions via the Fenton mechanism or by reacting directly on the electrocatalyst surface. Elimination of PEM chemical degradation is difficult due to constraints in terms of membrane materials, choice of fuel and oxidant, and fuel cell operating conditions. Therefore, it is imperative to develop effective mitigation strategies that minimize the rate and extent of PEM degradation.

There have been numerous approaches adopted to minimize PEM degradation. These include: i) lowering the number of reactive end groups or eliminating those reactive end groups in polymer membranes; ii) reducing the gas crossover across the membrane, thereby minimizing H_2O_2 and ROS generation; iii) optimizing fuel cell operating conditions; and iv) using free radical scavengers embedded within the membrane electrode assembly (MEA).^{3,4} By carefully tuning these approaches one can minimize, but never eliminate ROS-assisted PEM degradation. Only the complete and quantitative scavenging of the ROS generated in-situ during PEFC operation can mitigate PEM degradation with high efficacy. CeO_2 has been previously used as a free radical scavenger to mitigate the ROS-induced chemical degradation of PEMs.^{5,6} Though CeO_2 has been shown to scavenge ROS generated, its scavenging efficacy declines with time and is not truly regenerative (as desired)⁷. In our immediate past work, the ROS scavenging efficacy of commercially obtained CeO_2 particles within the PEM of an operating PEFC was precisely measured for the very first time using in-situ fluorescence spectroscopy.⁷ While the CeO_2 effectively scavenged radicals for the first 7 hours, its scavenging efficacy subsequently declined and 100% capture of ROS was not achieved after this point in time. The structural stability and free radical scavenging activity of cerium oxide (CeO_2) nanoparticles were improved by tuning its microstructure via nitrogen doping (N-doping).

Experimental

Commercially available CeO_2 (60 m^2/g) and high-surface-area CeO_2 (synthesized in-house; 220 m^2/g) were doped with nitrogen by annealing in the presence of a nitrogen rich atmosphere. The evolution of CeO_2 microstructure in Nitrogen doped (N-doped) commercial CeO_2 (20 m^2/g) and N-doped high-surface-area CeO_2 (90 m^2/g) was probed using transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, x-ray diffraction (XRD), and x-ray absorption spectroscopy (XAS).

In-situ fluorescence spectroscopy was employed to determine the regenerative ROS scavenging efficacy of all CeO_2 samples. Details of the in-situ fluorescence method and setup have been described in detail in our previous work.⁷

Results and Discussion

XPS and Raman measurements revealed that N-doping of CeO_2 enhanced the surface concentration of Ce^{3+} and concomitantly increased surface non-stoichiometry

(surface oxygen vacancy concentration) in both commercial CeO_2 and high-surface-area CeO_2 . XRD analysis of the doped samples revealed that the nitrogen atom replaced the oxygen atom in the CeO_2 lattice and that a lower electron density region prevailed around the N-doped sites. The high-surface-area CeO_2 and its N-doped version had significantly larger lattice parameters (5.4189 Å and 5.4192 Å respectively) than that of commercial CeO_2 and its doped version.

XAS studies revealed that the N-doped high-surface-area CeO_2 retained its active Ce^{3+} active clusters upon exposure to reactive oxygen species (ROS), thereby exhibiting excellent stability. The regenerative ROS (hydroxyl radical) scavenging ability of N-doped CeO_2 nanoparticles within the polymer electrolyte membrane (PEM) of an operating polymer electrolyte fuel cell (PEFC) was estimated using in-situ fluorescence spectroscopy. Experiments performed at 90 °C and 50% relative humidity yielded 100% regenerative radical scavenging efficacy in both N-doped commercial CeO_2 and N-doped high-surface-area CeO_2 for 40 hours of operation. (See Figure 1). However, while the N-doped commercial CeO_2 showed a decrease in scavenging ability after 40 hours, the N-doped high-surface-area CeO_2 showed at least 100 hours efficient and quantitative ROS scavenging, at which point the experiment was stopped. This study unequivocally demonstrates that structurally tuned nitrogen-doped CeO_2 nanoparticles exhibit superior regenerative ROS scavenging activity in polymer electrolytes and correlates the positive impact of enhancement/retention of Ce^{3+} active clusters and surface oxygen vacancy concentration (induced via N-doping) on the efficacy of regenerative ROS scavenging.

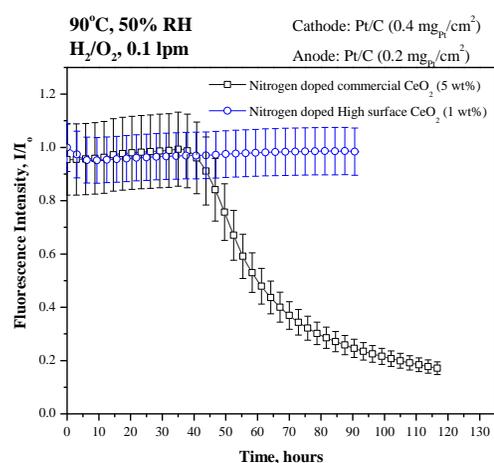


Figure 1: In-situ fluorescence spectroscopic estimation of regenerative ROS scavenging efficacy within the PEM of an operating PEFC upon addition of: (i) 5wt % N-doped commercial CeO_2 , and (ii) 1wt % N-doped high-surface-area CeO_2 . The experiments were performed at 90 °C and 50% RH under flowing H_2/O_2 at a flow rate of 0.1 lpm.

References

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