UV-Visible Spectroscopy Method for Screening the Chemical Stability of Potential Antioxidants for Proton Exchange Membrane Fuel Cells

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A novel method based on UV-visible spectroscopy is reported for screening the chemical stability of potential antioxidant additives for proton exchange membrane fuel cells, and the chemical stabilities of three CeO_x samples of varying crystallite sizes (6, 13, or 25 nm) are examined. The chemical stabilities predicted by this new screening method are compared to in-situ membrane electrode assembly (MEA) accelerated stress testing, with the results confirming that this rapid and inexpensive method can be used to accurately predict performance impacts of antioxidants.

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1. Introduction

To mitigate against free radical attack of the membrane in proton exchange membrane fuel cells (PEMFCs), free radical scavengers (e.g. oxides/salts of manganese or cerium) can be used[1-5]. While these additives greatly prolong the lifetime of the membrane, recent work has demonstrated that they can dissolve, with the resulting cations accumulating in the cathode catalyst layer (CCL)[6-8]. These cations bind with the ionomer's sulfonate groups in the CCL, resulting in greatly reduced proton availability and thus greatly reduced end of test (EOT) performance.

While fast screening techniques (e.g. Fenton's tests) are commonly used to predict the ability of antioxidants to function as free radical scavengers[2, 9], there are presently no screening methods for evaluating how stable these additives will be in the PEMFC environment. Thus, the stability of any potential new antioxidant materials must be evaluated in-situ, with full cathode or anode accelerated stress tests (ASTs) being performed[8]. Unfortunately this can be both time consuming and expensive, and is therefore a bottle-neck in the development and understanding of new antioxidants. Ideally, any ex-situ stability test for antioxidant materials would provide information not just on chemical stability, but also on the relative ratios of cations (e.g. $\text{Ce}^{3+}/\text{Ce}^{4+}$) that are released, as this ratio may impact the efficiency of the free radical scavenging of these additives[4].

In this work, we demonstrate that by using a recently developed[3] UV-visible spectroscopy method to monitor the dissolution of antioxidants in 1 M H_2SO_4 , reliable predictions can be made regarding the stability of these materials in a membrane

electrode assembly (MEA), thus allowing for accurate predictions on EOT performance. Using this method, three different CeOx samples were evaluated, having crystallite sizes of 6, 13, or 25 nm. To verify that the measured differences in chemical stabilities will translate into differences in the observed EOT performance following MEA ASTs, in-situ testing is carried out on MEAs containing the three different CeOx additives. In addition, a detailed voltage loss breakdown analysis is performed to help uncover the primary mechanism of performance loss for the MEAs containing CeOx.

2. Experimental Methods

2.1 Synthesis

The synthesis of the CeOx additives was based on a previously reported approach. Briefly, cerium acetate was dissolved in HNO₃, followed by the addition of NH₄OH. The samples were then calcined at 200, 600, 800 °C (LANL-200, LANL-600, and LANL-800 °C). For further details, the reader is directed to our previous work[7].

2.2 Physical Characterization

The UV-visible spectroscopy was performed using a Hitachi U-2900 spectrophotometer and Hellma 10 mm cuvettes. All scans were performed from 250-600 nm. Standard solutions were prepared using Ce(SO₄)₂, Ce(NO₃)₃, MnSO₄, Mn(C₅H₇O₂)₃ (Aldrich). X-ray diffraction spectra and gas sorption analysis were also performed (see references [3, 7] for further details).

2.3 MEA Testing

For MEA testing, the CeOx additives (loadings of 0.006 mg/cm²) were dispersed in an alcoholic Nafion ionomer solution, and then sprayed onto the anode catalyst layer

prior to assembling the MEA. This resulted in two separate layers (i.e. a Pt/C/ionomer layer and a CeOx/ionomer layer). The MEAs are referred to as MEA-LANL-X °C, where X is the calcination temperature used during the synthesis. All MEAs included carbon-based gas diffusion layers (GDL) and Nafion membrane. The catalyst layers were comprised of 23 wt% Nafion with anode and cathode Pt catalyst loadings of 0.1 and 0.4 mg/cm², respectively. For MEA performance evaluation, research-scale test cells (active area of 50 cm²) were used, and the operating conditions were 75 °C, 136 kPa, and 100% inlet RHs. Cathode AST cycling was performed under the same conditions, but at 80 °C. Square wave potential cycling was performed with a lower potential limit (LPL) of 0.6 V for 30 s and an upper potential limit (UPL) of 1.3 V for 60 s. CO stripping cyclic voltammetry (CV) was performed in-situ to estimate the electrochemical catalyst surface area (ECSA) during beginning of test (BOT), middle of life (MOL) and EOT testing. In-situ electrochemical impedance spectroscopy (EIS) was also performed at BOT, MOL and EOT. Details can be found in our previous work[7].

3 Results and Discussion

3.1 Ex-situ Testing of CeOx

XRD was used to evaluate the crystallite size of the three CeOx samples synthesized using a calcination temperature of 200, 600, or 800 °C. To estimate the crystallite size of the samples, the Scherrer equation was applied to the CeO₂ (111) peak. As expected, the crystallite size was found to increase with increasing calcination temperature (Table 1).

To probe the porosity of the CeOx samples, gas sorption analysis was performed. Importantly, micropore (t-plot) analysis demonstrated that none of the CeOx samples contained micropores, which ensures that any differences in the chemical stability of the

CeOx samples is purely due to differences in particle size rather than differences in porosity. Assuming that the crystallite size is a reflection of the actual particle size, and since the samples were found to be non-porous, the specific surface area was expected to decrease as calcination temperature increased. This is exactly what was observed, as shown in Table 1, with the measured surface area increasing in the following order: LANL-800 °C < LANL-600 °C < LANL-200 °C.

Prior to performing any dissolution studies on the CeOx additives, it was imperative to first demonstrate that UV-vis could be used to accurately measure the individual concentrations, and total concentration, of Ce cations in solution. Thus, initial work focused on performing UV-vis studies on two stock solutions of Ce^{3+} and Ce^{4+} with concentrations of 1 mM and 0.1 mM respectively. The Ce^{4+} stock solution was 10 x more dilute vs. the Ce^{3+} solution because of the much stronger absorption of UV radiation by Ce^{4+} vs. Ce^{3+} . From these stock solutions, three additional solutions were made by combining the solutions in a 3:1, 1:1, or 1:3 ratio (Ce^{4+} stock solution: Ce^{3+} stock solution). The resulting UV-vis spectra are shown in Fig. 1 (a).

It is clear from the UV-vis spectra of the two stock solutions (Fig. 1 (a)) that Ce^{3+} and Ce^{4+} absorb at different wavelengths ($\text{Ce}^{4+} = 320$ nm, $\text{Ce}^{3+} = 253$ and 295 nm) in 1 M H_2SO_4 . Also, the UV-vis spectra for the mixed $\text{Ce}^{3+}/\text{Ce}^{4+}$ solutions gradually change from Ce^{4+} -like to Ce^{3+} -like as the concentration of Ce^{3+} is increased. These two important observations suggest that it should be possible to deconvolute the individual concentrations of Ce^{3+} and Ce^{4+} from a solution of unknown $\text{Ce}^{3+}/\text{Ce}^{4+}$ concentration using UV-vis and stock solutions of Ce^{3+} and Ce^{4+} . To verify that the individual concentrations of Ce^{3+} and Ce^{4+} can be accurately predicted, theoretical spectra were generated for the mixed $\text{Ce}^{3+}/\text{Ce}^{4+}$ solutions through a 3:1, 1:1, or 1:3 ($\text{Ce}^{4+}:\text{Ce}^{3+}$) linear

combination of the original stock solutions. As shown in Fig. 1 (a), an excellent correlation was obtained between the predicted and measured spectra for the mixed $\text{Ce}^{3+}/\text{Ce}^{4+}$ solutions. Thus, by knowing the original concentrations of the stock solutions, the individual concentrations of Ce^{3+} and Ce^{4+} in an unknown solution can be solved analytically through a linear combination of the absorbance spectra for the stock solutions. Along with CeOx, MnO_2 is another commonly used antioxidant[10]. Thus, the same data, but for a mixture of Mn^{2+} and Mn^{3+} , was generated, and is shown in Fig. 1(b). Like the CeOx data, it is clear that the individual concentrations of Mn^{2+} and Mn^{3+} in an unknown mixture of the two cations can be accurately determined using this method.

Following this work, dissolution studies on the three LANL CeOx samples were performed by placing each of the samples in 1 M H_2SO_4 , and letting the samples settle overnight. After settling, the samples were each heated at 50 °C over a period of three days, with aliquots removed at the end of each day and measured with UV-vis. Best-fit linear combinations of the UV-vis spectra of the stock solutions to the UV-vis spectra of the solutions resulting from the dissolution study were obtained, allowing for accurate calculations of the $[\text{Ce}^{3+}]$ and $[\text{Ce}^{4+}]$ generated from the LANL CeOx samples. It is well known that CeOx nanoparticles consist of both Ce_2O_3 and CeO_2 [11, 12]. Thus, the Ce^{3+} cations were assumed to be due to dissolution of Ce_2O_3 and the Ce^{4+} cations were assumed to be due to dissolution of CeO_2 . This allowed for a calculation of the total mass of CeOx dissolved over a period of three days. As would be expected, the total mass dissolved was found to increase with decreasing particle size, likely due to the higher exposed surface area of the smaller CeOx particles (Table 1).

Clearly, the newly developed method predicts that the stability of the CeOx samples increases as: LANL-200 °C < LANL-600 °C < LANL-800 °C. Previous work has

demonstrated that MEAs containing antioxidants suffer from rapid performance degradation during anode or cathode ASTs, with this performance degradation typically attributed to dissolution of the antioxidant resulting in accumulation of cations in the CCL[6-8]. Therefore, in-situ testing of the CeOx samples not only can be used to validate the newly developed UV-vis method, but if the predicted trends are observed, can provide extremely convincing evidence that dissolution of the antioxidants is responsible for rapid performance loss.

3.2 In-situ Testing of CeOx

Three MEAs were prepared, with LANL-200 °C, LANL-600 °C, or LANL-800 °C sprayed onto the anode catalyst layer, each at a loading of 0.006 mg/cm². For comparison, a baseline MEA containing no CeOx was also prepared. As is shown in Fig. 2, the CeOx additives have no impact on BOT performance. However, previous work by our group[8] has demonstrated that losses due to antioxidants are accelerated when the cathode catalyst layer is degraded. Therefore, cathode AST cycling from 0.6-1.3 V was performed on each of the three MEAs. During this AST, it is known that Pt dissolution, Pt agglomeration, Ostwald ripening, and carbon corrosion can occur, leading to performance losses[13]. These well known mechanisms for performance loss are clearly experienced by the baseline MEA, resulting in lower EOT vs. BOT performance (Fig. 2). However, by comparing the EOT performance of the baseline MEA to those of the MEAs containing CeOx, it is possible to identify the additional performance losses that are experienced as a result of CeOx dissolution. Importantly, the EOT performances of the MEAs containing CeOx (Fig. 2) clearly trend in the same order as the chemical stabilities predicted by the newly developed UV-vis method (Table 1), providing

validation not only of this new method, but also convincing evidence that dissolution of the antioxidants has a significantly adverse impact on performance.

As Ce cations accumulate in the CCL, proton transport is hindered, resulting in an increase in ionic resistance through the layer. Thus, to verify that the EOT performance losses of the CeOx-containing MEAs shown in Fig. 2 are truly due to accumulation of cations in the cathode catalyst layer, a voltage loss breakdown analysis (developed in-house[14]) was used to determine the CCL ionic losses. Briefly, this analysis uses the polarization data, as well as the EIS data, to determine the individual contributions from kinetic, ohmic, and mass transport overpotentials. As is shown in Fig. 3 (a), the CCL ionic losses follow the same trend as the EOT performances, providing further evidence that dissolution of these additives is the cause of the large EOT performance losses that are observed. While it is also possible that the dissolved Ce cations could contaminate the membrane, leading to increased ohmic losses, it is clear from Fig. 3 (b) that this does not appear to be a dominant loss among the three CeOx samples. Although LANL 200 °C shows slightly higher ohmic losses vs. the other three MEAs, there is no clear trend between the observed ohmic losses and the EOT performance of the MEAs. Thus, the evidence strongly suggests that the primary mechanism of performance loss is contamination of the CCL by the dissolved CeOx additives.

4. Conclusions:

A new method based on UV-visible spectroscopy was developed for screening the chemical stability of antioxidants for use in PEMFCs. It was shown that theoretical UV-vis spectra obtained through 3:1, 1:1, or 1:3 linear combinations of the UV-vis spectra of $\text{Ce}^{4+}:\text{Ce}^{3+}$ or $\text{Mn}^{2+}:\text{Mn}^{3+}$ stock solutions overlay with a nearly perfect fit to the

experimental UV-vis spectra for these solutions. Thus, it is possible to analytically solve the individual concentrations of $\text{Ce}^{3+}/\text{Ce}^{4+}$ or $\text{Mn}^{2+}/\text{Mn}^{3+}$ in unknown solutions using this approach. To evaluate this method, three CeOx samples were synthesized using calcination temperatures of 200 (LANL-200 °C), 600 (LANL-600 °C), or 800 °C (LANL-800 °C), with crystallite sizes of 6, 13, or 25 nm respectively. Using this method, the total mass dissolved of the three CeOx samples over a period of three days at 50 °C in 1 M H_2SO_4 samples was found to be: LANL-200 °C = 13 mg, LANL-600 °C = 4.6 mg, LANL-800 °C = 0.28 mg. Finally, in-situ MEA accelerated stress testing (AST) of MEAs containing the CeOx additives (as well as a baseline MEA) was performed, with end of test performances matching perfectly with the predicted trend based on the chemical stabilities of the three CeOx samples as measured through this new method (LANL-200 °C < LANL-600 °C < LANL-800 °C). Through a detailed voltage loss analysis, the primary mechanism for the observed performance loss of the MEAs containing CeOx was found to be contamination of the cathode catalyst layer by Ce cations.

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Table 1 Physical properties and measured dissolution of the LANL CeOx samples

Sample	Crystallite size from XRD(111) $\pm$ 0.5 nm	BET Surface area (m²/g) $\pm$ 5 %	Mass Dissolved after 3 days (mg)^a $\pm$ 10 %
LANL-200 °C	6	98	13
LANL-600 °C	13	30	4.6
LANL-800 °C	25	9	0.28

^a As determined by UV-vis, following three days of heating at 50 °C in 1 M H₂SO₄.

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Figure 1: (a) (i-v) Experimentally measured UV-vis spectra for the five solutions of Ce³⁺/Ce⁴⁺. Curve (vi) shows a UV-vis spectra generated through a linear combination of the two Ce-based stock solutions. (b) Experimentally measured UV-vis spectra for the five solutions of Mn²⁺/Mn³⁺. Curve (vi) shows a UV-vis spectra generated through a linear combination of the two Mn-based stock solutions. All Ce and Mn cation solutions were prepared in 1 M H₂SO₄. Fig. 1 (a) is adapted with permission from J. Electrochem. Soc., 161, F1075 (2014). Copyright 2014, The Electrochemical Society

Figure 2: (a) BOT and EOT performance plots for the three MEAs containing the LANL CeOx additives (0.006 mg/cm² CeOx loadings). Performance plots obtained at Temperature: 75 °C, Pressure: 136 kPa, Inlet RH: 100 %, Fuel/oxidant: H₂/Air.

Figure 3: (a) Cathode catalyst layer ionic losses vs. the number of cathode potential cycles from 0.6-1.3 V. (b) Ohmic losses vs. the number of cathode potential cycles from 0.6-1.3 V.