

# Greener Method to a Manganese Oxygen Reduction Reaction Electrocatalyst: Anion Electrolyte Effects on Electrocatalytic Performance

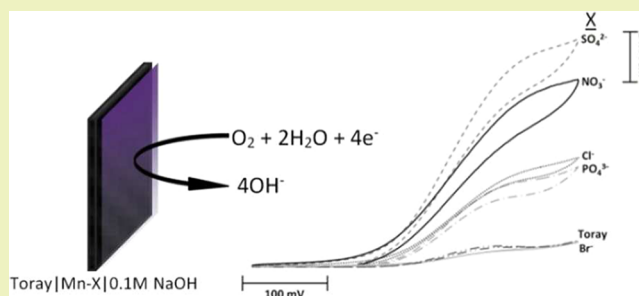
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## S Supporting Information

**ABSTRACT:** Efforts to reduce the cost of production and reduce hazards associated with catalyst production, as well as improve catalytic performance of fuel cells, is increasingly gaining attention in chemistry, materials science, and chemical engineering. Costs, particularly of the catalyst system, are incurred in each step of production, including raw materials and their processing, catalyst preparation, and immobilization on electrodes. Here is described a low-temperature neutral pH method of electrodepositing a manganese oxygen-reducing electrocatalyst for alkaline fuel cell systems. The analysis emphasizes the effects of anions used during the deposition process and their effect on catalytic performance.

**KEYWORDS:** Electrocatalyst, Electrochemistry, Fuel cell, Oxygen reduction reaction, Alkaline



## INTRODUCTION

Manganese and its oxides (e.g., MnO, MnO<sub>2</sub>, and MnOOH) are ubiquitous in electrochemical energy systems. Manganese is an earth abundant and environmentally safe metal, employed in batteries<sup>1</sup> and high power density capacitors<sup>2</sup> and more recently as an alternative to platinum group metal electrocatalysts for the oxygen reduction reaction (ORR).<sup>3–10</sup> These applications are the result of complex and diverse chemical and electrochemical properties, as Mn exists in many polymorphs (as described by De Wolf<sup>11</sup>) and many oxidation states. The use of MnO<sub>2</sub> as an electrocatalyst, specifically for oxygen reduction is not new<sup>12</sup> but has gained increasing attention as an alternative to platinum catalysts in alkaline fuel cells,<sup>9</sup> as the alkaline fuel cell research has expanded over the last 5 years.

Often, these MnO<sub>2</sub>-based catalysts systems require multiple chemical, thermal, and mechanical processes for electrode fabrication.<sup>3,4,7,8</sup> The chemical oxidation in strong acid solutions (H<sub>2</sub>SO<sub>4</sub>)<sup>13</sup> of MnO<sub>2</sub> precursors, such as MnO, KMnO<sub>4</sub>, and MnSO<sub>4</sub>, are often followed by thermal treatment or pyrolysis. Resultant powders then require milling for uniformity and subsequent pressing or rolling onto current collectors of nickel, stainless steel, or carbon, followed by additional thermal treatment to achieve mechanical stability and cohesion with conductivity additives (e.g., graphite or vulcanized carbon).

Group IV electrocatalysts have, alternatively, often been prepared via electrodeposition techniques. These materials display catalytic performance in alkaline media nearing their platinum group metal counterparts.<sup>5,9,10</sup> Electrodeposition eliminates the need for thermal and mechanical steps, as

deposition occurs on materials directly applied to the power source (e.g., carbon paper for air breathing cathode). These electrocatalysts, comprised of other metals such as nickel and cobalt, are increasingly being studied for their use as oxidative electrocatalysts, with high catalytic efficiency of fuel (e.g., aliphatic alcohols)<sup>14–16</sup> and water oxidation in alkaline solutions.<sup>17–19</sup> However, of particular interest are the rarely studied effects of supporting electrolyte (deposition bath electrolyte) anions and their effect on catalyst performance. Few examples are found in the literature, but of those that exist are copper–sulfates<sup>20,21</sup> and cobalt–phosphates. Indeed, work by the Nocera group on Ni–Pi and Co–Pi is pioneering in the field of nonplatinum group (NPG) electrocatalysts.<sup>17–19,22</sup> These are complementary but in contrast to studies that consider codeposited metal species as catalytic materials.<sup>10,23</sup>

Here, we have set out to analyze the effects of anions on manganese oxygen reduction electrocatalysts, which have previously not been evaluated. Unlike the aforementioned oxides of manganese, this electrode preparation method requires only electrodeposition from low concentration MnCl<sub>2</sub> solutions with no subsequent thermal or mechanical treatments. To the best of our knowledge, the only other study considering Toray electrode substrates for manganese electrocatalysts was the recent study by Gyenge et al., who utilized various commercial sources of manganese dioxide and considered the effects of hydrophobic Teflon coatings on

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Toray paper.<sup>4</sup> Our results show that a substantial and significant effect is observed though the use of different electrolyte compositions and concentrations. A comparison is made to more traditionally prepared  $\text{MnO}_2$ , i.e., deposition of  $\text{MnSO}_4$  oxidation at elevated temperatures (85 °C) in 0.1 M  $\text{H}_2\text{SO}_4$ . The experimental results demonstrated herein show statistically significant differences in oxygen reduction catalysis of manganese deposited from a variety of neutral pH anion-supporting electrolytes. Additionally, the results demonstrate that manganese deposited from neutral sulfate solutions catalyze ORR in alkaline equivalently to acid prepared Mn species, which shows that this greener method can be utilized for fabricating equivalent electrocatalysts.

## EXPERIMENTAL SECTION

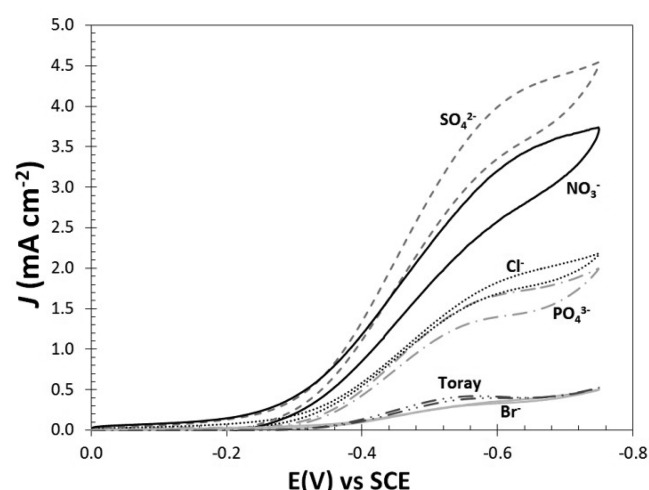
Electrocatalysts are prepared via an amperometric deposition method from low concentration solutions of  $\text{MnCl}_2$  (0.5 mg/mL, Aldrich, flakes 97%) in 18 M $\Omega$  water (Milli-Q) with the appropriate electrolyte and concentration. Anions from supporting electrolytes of phosphate ( $\text{K}_2\text{HPO}_4$ , Fisher, anhydrous), chloride (NaCl, Fisher), bromide (NaBr, Fisher), nitrate ( $\text{KNO}_3$ , Mallinckrodt Chemicals), nitrite ( $\text{KNO}_2$ , Aldrich), sulfite ( $\text{KSO}_3$ , Aldrich), and sulfate ( $\text{K}_2\text{SO}_4$ , J. T. Baker) were examined for their effects on deposition. Deposition solutions of the various electrolytes examined were performed at 100 mM concentrations of anions, while the effects of concentration on deposition and catalytic properties were considered for sulfate anions over a range of 25 mM to 150 mM.

Electrodes are 1 cm<sup>2</sup> of Toray carbon paper. Amperometric deposition throughout the study proceeds for 30 min at 1.755 V vs SCE. An eight electrode array was fabricated as per the procedure in ref17 and allows for simultaneous deposition from a single manganese solution. A platinum mesh counter electrode and saturated calomel reference electrode (SCE) are used in conjunction with a Digilvy 2300 bipotentiostat for deposition and electrochemical analysis, where all electrochemical experiments are run as replicates ( $n \geq 3$ ). Primary electrochemical analysis consists of cyclic voltammetry (CV) performed in 0.1 M NaOH solutions at scan rates of  $\nu = 50$  mV sec<sup>-1</sup> over a potential range of 0.0–0.75 V vs SCE.

Surface characterization was performed via AFM and white light interferometry. The images for these analyses are given in the Supporting Information. Elemental composition was performed via XPS, AFM, XPS, and interferometry, which necessitates sample preparation on glassy carbon. The manganese electrocatalysts were prepared as described above but replacing Toray carbon paper with glassy carbon bars (2 cm × 0.3 cm × 0.1 cm).

## RESULTS AND DISCUSSION

Previous studies show that phosphate has a substantial beneficial effect on both nickel and cobalt electrocatalysts.<sup>17,18</sup> However, in the case of manganese, the electrodeposition of  $\text{Mn}^{2+}$  in the presence of phosphate does not improve the electrocatalytic properties of manganese. Phosphate counterion shows no significant difference in electrocatalysis between using phosphate or using chloride as the counterion, as shown in Figure 1. This result is consistent with  $\text{MnO}_2$  protocols via oxidation methods in acid, with and without thermal treatments.<sup>2,3,7,8,10,13,24</sup> The representative cyclic voltammograms in Figure 1 (a flooded cell containing 0.1 M NaOH and saturated with  $\text{O}_2(\text{g})$ ) show that  $\text{Mn}^{2+}$  deposited in the presence of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  reduces significantly more oxygen versus the presence of any other anion supporting electrolyte or the Toray paper control. The 0.1 M NaOH alkaline solutions were, for consistency, used throughout the analysis of the ORR at the manganese electrocatalysts. The concentration of hydroxide ions in alkaline electrochemical systems varies throughout



**Figure 1.** Representative cyclic voltammograms of the average current response ( $n = 4$ ) for various co-electrodeposited manganese species at a scan rate of  $\nu = 50$  mV sec<sup>-1</sup> in 0.1 M NaOH (aq).

literature; however, an analysis by Takashima et al. indicates the electrocatalytic activity of  $\text{MnO}_x$  ORR electrocatalysts is preserved at pH values  $\geq 9$ .<sup>25</sup> The corresponding data shown in Table 1 shows this catalytic turnover, where values are the

**Table 1.** Average Current Response of Various Co-Electrodeposited Manganese Species in 0.1 M NaOH aq Solutions Saturated with Either  $\text{N}_2(\text{g})$  or  $\text{O}_2(\text{g})$

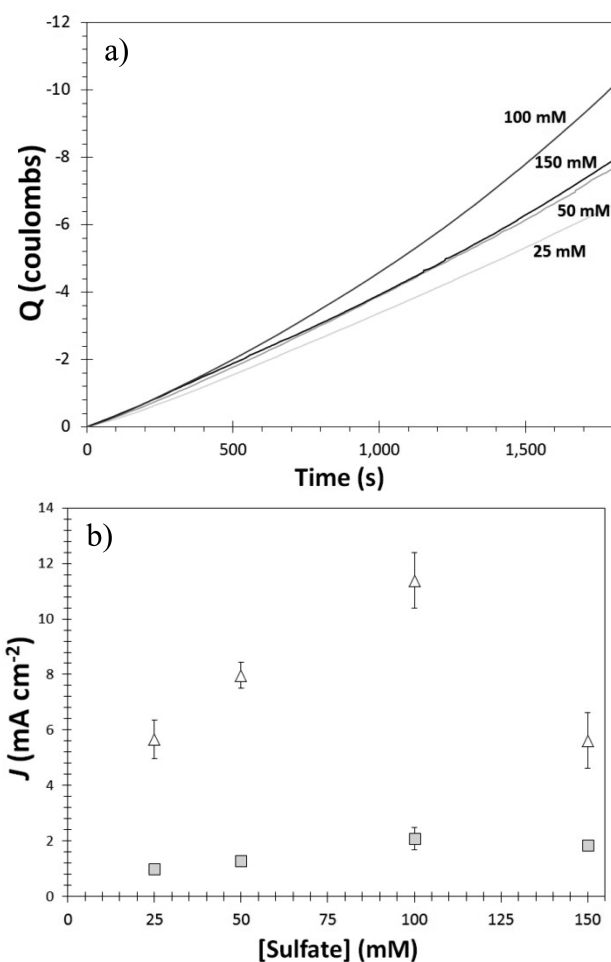
composition	$\text{N}_2/J$ (mA cm <sup>-2</sup> )	$\text{O}_2/J$ (mA cm <sup>-2</sup> )
Mn phosphate	0.39 ( $\pm 0.03$ )	1.67 ( $\pm 0.33$ )
Mn chloride	0.38 ( $\pm 0.13$ )	1.82 ( $\pm 0.46$ )
Mn bromide	0.05 ( $\pm 0.01$ )	0.36 ( $\pm 0.05$ )
Mn nitrate	0.61 ( $\pm 0.16$ )	3.20 ( $\pm 0.58$ )
Mn sulfate	0.59 ( $\pm 0.11$ )	3.99 ( $\pm 0.43$ )
Toray	0.05 ( $\pm 0.02$ )	0.39 ( $\pm 0.06$ )

\*Electrode deposition solutions prepared using 100 mM electrolyte solutions with 0.5 mg mL<sup>-1</sup>  $\text{MnCl}_2$ ; simultaneous deposition of  $n = 4$  electrodes at 1.755 V vs SCE for 1800 s.

average of four electrodes for the current density response ( $J$ ) at 0.6 V vs SCE and in the presence and in the absence of oxygen at Mn–Toray carbon paper electrodes. This may be a result of the added overpotential used during the deposition process, in contrast to the cycling potential window utilized in previously studied acid-based oxidation protocols.<sup>9,10</sup> Sulfate salt are often utilized as supporting electrolytes.<sup>9,10,20,21</sup> Likewise, the electrodeposition of manganese often uses acid sulfates (i.e.,  $\text{H}_2\text{SO}_4$ ). However, the anion's impact on catalytic performance is not documented, that is to say, the specific mechanism for this impact is not a well-understood or reported phenomenon.

It is interesting to note that no apparent periodic trends exist for this behavior. The electrolyte effects examined showed no sensitivity to the counterion of the electrolyte, that is, salts of sodium and potassium to behave similarly (data not shown). The composition of the nonoxygen species (i.e., S in  $\text{SO}_4^{2-}$ , etc.) used for deposition was also considered. Salts of nitrite ( $\text{NO}_2^-$ ) and sulfite ( $\text{SO}_3^{2-}$ ) were used for comparison, but when codeposited with  $\text{Mn}^{2+}$  were catalytically outperformed by both  $\text{Cl}^-$  and  $\text{PO}_4^{3-}$  manganese species, as shown in Figure S1 of the Supporting Information.

The effects of supporting electrolyte concentration on catalytic performance were also considered. Holding the concentration of manganese constant, Mn-SO<sub>4</sub> species were deposited over a range of 25–150 mM Na<sub>2</sub>SO<sub>4</sub> solutions. Figure 2a shows the deposition curves. The corresponding

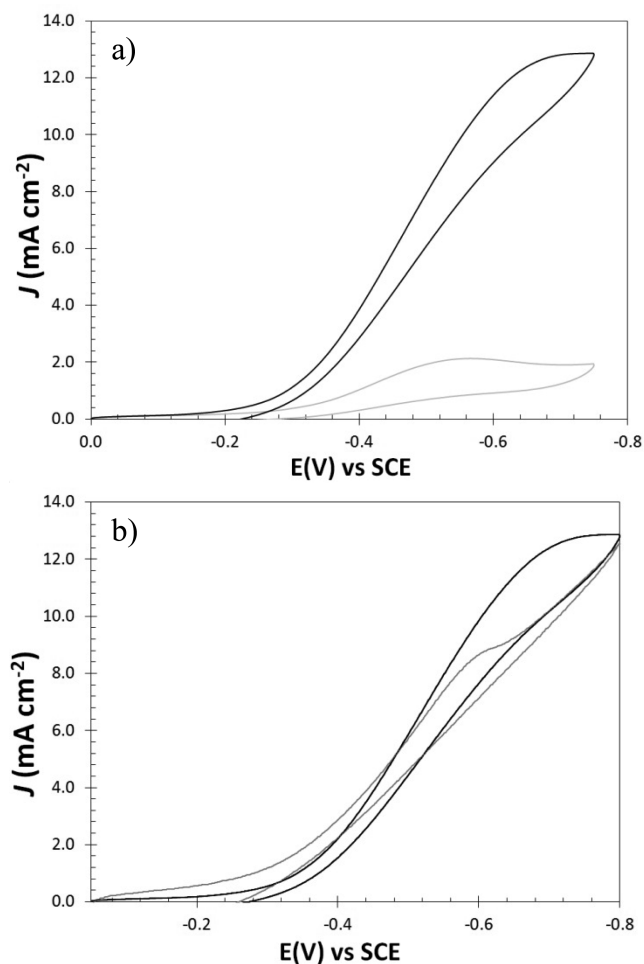


**Figure 2.** (a) Deposition curves of manganese deposited with varying concentrations of Na<sub>2</sub>SO<sub>4</sub> (aq) at 1.755 V vs SCE. (b) Current responses of manganese sulfate electrocatalysts, response collected at 0.6 V vs SCE in the presence of O<sub>2</sub> (g) (triangles) and N<sub>2</sub> (g) (squares),  $\nu = 50 \text{ mV sec}^{-1}$  for  $n = 3$  electrodes.

catalytic response for the ORR at 0.6 V vs SCE is shown in Figure 2b. It should be noted that the current response for Figures 2 and 3 are the average current density ( $J$ ) for  $n = 3$  electrodes simultaneously deposited. The number of electrodes simultaneously deposited affects the magnitude of current response and the corresponding catalytic performance.

ORR electrocatalysis and the amount of charge passed during deposition trend linearly between 25 and 100 mM SO<sub>4</sub><sup>2-</sup>, and it is safe to assume a Faradaic behavior exists. However, beyond 100 mM, the additional charge is likely attributed to deposited SO<sub>4</sub><sup>2-</sup> rather than increased manganese deposition. The lack of selectivity afforded by amperometry necessitates spectroscopic analysis of the final product. XPS was used here for this analysis.

Above 100 mM sulfate, the majority of the deposited species (and charge) is likely attributed to SO<sub>4</sub><sup>2-</sup>, as the catalytic performance of manganese electrodes prepared in 50 mM sulfate solutions is increased 40% ( $7.9 \pm 0.4 \text{ mA cm}^{-2}$  versus



**Figure 3.** Voltammetric response of oxygen reduction at Mn sulfate electrocatalyst on Toray electrodes in 0.1 M NaOH aq solutions, scan rate  $\nu = 50 \text{ mV sec}^{-1}$ . (a) Average current response of 0.1 M K<sub>2</sub>SO<sub>4</sub> deposited electrodes with O<sub>2</sub> (black) and N<sub>2</sub> (gray). (b) Average current response of 0.1 M K<sub>2</sub>SO<sub>4</sub> deposited electrodes (black) and 0.1 M H<sub>2</sub>SO<sub>4</sub> deposited electrodes (gray).

$5.6 \pm 1.1 \text{ mA cm}^{-2}$ ), indicating a competitive deposition process. This is further confirmed by the average increased capacitance in degassed solutions at 50 mM versus 150 mM sulfate deposited electrodes.

A comparison to more traditionally prepared MnO<sub>2</sub> electrocatalysts was performed. For the analysis, electrodes were prepared under analogous conditions: 0.5 mg/mL MnSO<sub>4</sub>, 0.1 M H<sub>2</sub>SO<sub>4</sub>, 1800 s electrodeposition at 1.755 V vs SCE, and  $n = 3$  electrodes. Figure 3b gives a comparison of average current response for oxygen reduction between the two deposition protocols. Onset of oxygen reduction is at approximately the same potential, while the character of current response is almost identical until the diffusion limited behavior of the K<sub>2</sub>SO<sub>4</sub> species occurs at  $\sim 0.7 \text{ V vs SCE}$ . The wave at 0.6 V is a result of diffusion limited character (approximately  $8 \text{ mA cm}^{-2}$ ) for one sample; a high amount of variance was observed when electrodes were electrodeposited in acid at 85 °C.

A comparison to more traditional Pt electrocatalysts should also be made. As current density measurements are highly variable and system dependent, a comparison to onset potentials is appropriate. At previously studied planar platinum, in 1 M KOH the ORR occurs at  $-0.25 \text{ V vs Hg/HgO}$  (1 M).

Accounting for reference electrode and  $[\text{OH}^-]$ , this value shifts to  $-0.185\text{ V}$  vs SCE in  $0.1\text{ M}$  hydroxide ions.<sup>26</sup>

Surface characterization and elemental composition were also considered on the two most well-performing materials, Mn sulfate and Mn nitrate, in order to associate chemical composition and oxidation state to electrocatalytic function, as well as indicating any possible structure–function relationships. White light interferometry and AFM were used to characterize surface structure of the Mn deposits, and XPS was used for elemental analysis. Given the constraints of these techniques, atomically flat sample substrates are required for AFM and interferometry, and a reflective surface is also required for interferometry. As such, it was necessary to substitute glassy carbon bars for the Toray carbon paper traditionally used for fuel cell supports.<sup>27</sup>

Both AFM and interferometry reveal a highly roughened surface (the carbon is highly polished and flat before deposition (roughness =  $1.26\text{ nm}$ )). Interferometry (Figure S2, Supporting Information) indicates that pitting (depths of  $3\text{ }\mu\text{m}$ ) of the carbon surface occurs during deposition for both Mn– $\text{SO}_4$  and Mn– $\text{NO}_3$ ; a similar mechanism may occur on Toray, roughening an already high surface area material. Interferometry also reveals excessive fracturing on the macroscale of the deposited material for the Mn– $\text{SO}_4$  sample. AFM measurements (Figure S3, Supporting Information) of structures between pits reveal large substructures, on the order of  $175\text{ nm}$  in height on average for Mn– $\text{SO}_4$ , with similar structures for the Mn– $\text{NO}_3$ . The average roughness of the Mn–sulfate is  $R_q = 26.2\text{ nm}$ , while for Mn–nitrate the RMS roughness is  $R_q = 7.31\text{ nm}$ . This is an interesting result when the elemental composition data is considered. XPS (Figure S4, Supporting Information) reveals the mass percent of Mn (as Mn 2p) in the Mn–nitrate deposited sample is at  $49.26\%$  with atomic percentage at  $16.53\%$ , while the Mn in the Mn–sulfate sample is at a mass percent of  $42.99\%$  and atomic concentration at  $20.71\%$ . These results indicate that the manganese content in the electrocatalyst is not the primary feature for high catalytic turnover of ORR. The electrolyte and its composition may be performing a dual role, affecting both Mn deposition and catalysis of the ORR.

Rationalizing this effect is not straightforward. Changing the electrolyte may merely be affecting interfacial activities between the solvent layer and electrode surface at the electrochemical double layer. This change may affect the energy required for solvent reorganization energy at the double layer during manganese deposition. Adsorbates are necessary in many chemical processes that occur at electrode interfaces, such as the evolution of molecular hydrogen and oxygen. Gileadi offers insight into metal deposition and the need for surface adsorbates.<sup>28,29</sup> As Gileadi states, during metal deposition, the solvated cation needs to lose its solvation shell and transfer the electron to the electrode surface. This two-step charge transfer process likely occurs though an ionic species adsorbed at the electrode surface. The final products deposited in this study were identified as  $\text{MnO}_2$  by XPS, a result consistent with literature. However, unlike metal deposition via reduction (i.e.,  $\text{Mn}^{n+}_{\text{solution}} + ne^- \rightarrow \text{M}^0_{\text{adsorbed}}$ ), here it is assumed that deposition occurs via manganese oxidation and complex to anions in solution, more consistent with the use of complexing agents (e.g., citrate).<sup>30</sup> If Gileadi's theory hold true that surface adsorbates facilitate deposition via a mechanism of charge transfer, it may be that complex formation is also adsorbate dependent, and this may be the effect that is observed.

Likewise, it may be that the electrolyte performs two functions: to both affect the deposition by providing a medium for charge transfer and to lower the energy required for solvent reorganization. Continuing analysis of this system and these electrolyte effects on metal deposition are ongoing. Analyses through combining electrochemical techniques with spectroscopy techniques using Raman or Auger spectroscopy in situ during electrochemical deposition are warranted to analyze this phenomenon.

## CONCLUSIONS

This study demonstrates the merit of electrodeposited manganese on high surface area Toray carbon paper electrodes as a facile and “greener” means of creating oxygen reduction catalysts for alkaline fuel cell applications. A stark difference in catalytic performance is observed depending upon the anion of the supporting electrolyte used during deposition, where catalytic performance for the ORR followed the trend of  $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{PO}_4^{3-} > \text{control} > \text{Br}^-$ . Trends in the behavior of the electrolyte on electrocatalysis are not forthcoming; however, deposition curves indicate the importance of electrolyte concentration on catalytic performance. A structure–function relationship may account for this difference in performance given the high degree of roughness observed via AFM and interferometry; however, the difference in Mn deposited is slight. Further investigation into the four electron reduction mechanism is warranted, as is the mechanism of deposition of manganese in various electrolytes. The use of different electrolytes may affect deposition through activity effects, or it may be that the different chemical species promote the deposition of varying phases of manganese. Rotating ring disk electrode (RRDE) experiments studying oxygen reduction and spectroelectrochemical analysis of catalyst formation are underway.

## ASSOCIATED CONTENT

### Supporting Information

AFM and white light interferometry surface characterization data and XPS elemental data, as well as the experimental procedures for each. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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