Electrocatalyzed Oxygen Reduction at Manganese Oxide Nanoarchitectures: From Electroanalytical Characterization to Device- Relevant Performance in Composite Electrodes

Jesse S. Ko, Joseph F. Parker, Mallory N. Vila, Mason A. Wolak, Megan B. Sassin, Debra R. Rolison, and Jeffrey W. Long

1 Naval Research Laboratory, National Research Council Postdoctoral Associate, Washington, DC 20375, USA
2 U.S. Naval Research Laboratory, Surface Chemistry Branch (Code 6170), Washington, DC 20375, USA
3 U.S. Naval Research Laboratory, Surface Chemistry Branch (Code 5616), Washington, DC 20375, USA

We assess the effect of the pore–solid architecture of cryptomelane-type manganese oxide (MnOx) xerogels and aerogels on electrocatalysis of the oxygen-reduction reaction (ORR) using three different electrochemical test platforms. Rotating-disk electrode measurements at ink-cast films of carbon + MnOx show that both MnOx nanoarchitectures exhibit comparable intrinsic ORR activity for four-electron reduction with a low onset overpotential (~310 mV). The MnOx xerogel and aerogel powders were also incorporated into practical powder–composite electrodes that include carbon and polymer binder. When evaluated in an air-breathing three-electrode electroanalytical cell, the aerogel-based composite electrode exhibits an overpotential lowered by ~50 mV compared to the xerogel-based analog. The superior performance of the aerogel-based composite is also demonstrated in zinc–air button cells, with up to 100 mV improvement in discharge voltage at moderate-to-challenging current densities (5–125 mA cm⁻²). We ascribe the enhanced activity of the MnOx aerogel-based composite to a more uniform dispersion of the aerogel powder within the carbon/binder matrix, as verified by focused-ion beam—scanning electron microscopy and elemental mapping. The results reported herein highlight the importance of assessing the translation of electrocatalytic activity from fundamental measurements to technologically relevant electrode structures.

© The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.1351811jes]

Manuscript submitted July 20, 2018; revised manuscript received August 30, 2018. Published September 8, 2018.

Nanostructured manganese oxides (MnOx) are effective electrocatalysts in alkaline media for the oxygen-reduction reaction (ORR), thus serving a critical function in the air-breathing positive electrodes of zinc–air batteries and alkaline fuel cells. The ORR activity of MnOx depends on multiple factors including; specific crystalline structure, particle morphology, manganese valence as influenced by surface defects, and high specific surface area, either of the oxide itself or by incorporating it with high surface area carbon. A survey of the literature shows that both MnOx xerogels and aerogels were synthesized via established sol–gel methods. Supercritical CO₂ extraction of wet MnOx powders (after exchanging H₂O for acetone in the pores) generates the corresponding aerogel form. The MnOx xerogels and aerogels were heated for 2 h at 300 °C under static air, ramping to temperature at 2 °C min⁻¹. Powder X-ray diffraction was performed using a Rigaku SmartLab X-ray diffractometer with a Cu Kα (λ = 1.5406 Å) radiation source, scanning from 20–70° with a 0.02° step size and an integration time of 1 s per step. Nitrogen-sorption measurements were made using a Micromeritics ASAP 2020 porosimeter; samples were degassed for 12 h at 80 °C under vacuum prior to analysis. Scanning electron micrographs were taken using a Carl Zeiss Leo Supra MM microscope operating at 5 keV by affixing the MnOx powders and MnOx catalyst–carbon composite powders onto aluminum stubs with double-sided carbon tape. Elemental mapping was performed using energy-dispersive spectroscopy with the same instrument operated at 20 keV. Elemental analysis of the surface of xerogel and aerogel powders–composites was assessed using an X-ray photoelectron spectrometer (Thermo Scientific K-Alpha X-ray) equipped with a monochromatic Al Kα source (1486.68 eV) and a 400-μm elliptical spot size. High-resolution spectra over the C 1s, O 1s, Mn 2p, F 1s, and Zr 3d regions were obtained at an energy step-size of 0.1 eV. The instrument was operated with a low-energy electron flood gun and the resulting spectra were not peak-shifted prior to quantitative analysis. The spectra were analyzed with Avantage software version 5.35.

We previously reported the synthesis of cryptomelane MnOx in the form of sol–gel-derived nanoarchitectures with differing pore volume; aerogel (Ambigel) > xerogel > aerogel. These materials exhibit high specific surface area (>130 m² g⁻¹) whether expressed as a mesoporous xerogel or as a low-density aerogel. Yet, the performance of these two forms diverge once they are fabricated as powder–composite electrodes. The internal structure of the aerogel and xerogel powder–composites were imaged and analyzed using an FEI Helios NanoLab.
Dual beam fitted with an Oxford Instruments X-Max® 150 detector for energy-dispersive X-ray spectroscopy (EDS) measurements. Large-area focused-ion beam (FIB) milling into the sample was achieved with a Ga⁺ ion beam operating at 30 kV using a beam current of 2.5 nA. The initial excavation sites were typically 30-μm wide by 25-μm long with a depth of 15–20 μm. Final ‘cleaned’ cross sections for SEM imaging and EDS analysis were prepared by FIB milling at lower beam current (0.23–0.46 nA) to minimize damage to the region of interest. At least four different locations were milled and imaged on each sample, with representative cross sections chosen for display in the Zinc–Air Full Cell Performance Evaluation section. Cross sections were imaged with the Dualbeam SEM operating at 20 kV using a beam current of 3.2 nA. Identical electron beam setting were used during collection of EDS elemental mapping data, which were analyzed using the Oxford Instruments Aztec 2.2 software. The EDS spectra were obtained in the range of 0–20 keV and equivalent X-ray collection settings were used for analysis of both aerogel and xerogel powder–composite electrode samples.

Rotating disk electrode analysis.—Glassy-carbon rotating disk electrodes (RDE; 5-mm diameter, nominal area = 0.196 cm², Pine Instruments) were mirror polished using 1.0-μm and then 0.05-μm alumina slurries followed by rinsing with and sonication in 18 MΩ cm water, with a final sonication in isopropanol. Catalyst-modified RDEs were prepared by suspending 5 mg of a ground mixture containing equal masses of MnOₓ xerogel or aerogel catalyst and Vulcan XC-72 carbon (Cabot) in 3 mL of a solution containing Nafion perfluorinated resin (5 wt% solution of Nafion in aliphatic alcohols and water; Aldrich), isopropanol, and water at a v:v ratio of 0.4 vol% Nafion, 20 vol% isopropanol, and 79.6 vol% water. This suspension was then sonicated for 1 h, stirred for 1 h, and sonicated for an additional 1 h; 10 μL of this suspension was subsequently deposited onto an inverted glassy-carbon RDE and dried under ambient conditions.

Current–potential trends for electrocatalytic O₂ reduction (ORR) at the MnOₓ catalysts were obtained under continuous bubbling of O₂ using linear-sweep voltammetry at 10 mV s⁻¹, a scan rate that is sufficiently slow to reflect steady-state conditions. All potentials (applied and measured) were converted to overpotentials (η) relative to the thermodynamic potential using the equation:

\[ \text{E} = [1.23 - 0.138 - (0.059 \times \text{pH})] \text{V} \quad [1] \]

where 1.23 V vs. NHE is the potential for O₂ evolution at pH 7 and 0.138 V vs. NHE is the potential of the junction-isolated Hg/HgO reference electrode; the pH of the electrolyte (1 M KOH) was measured prior to each experiment using a Fisher Scientific AB15 pH meter. The counter electrode used for these measurements was a gold mesh. The potentials measured were compensated for iR loss based on resistance values determined from impedance at open-circuit potential.

Air-breathing half-cell electrode assessment.—Carbon–composite electrodes were prepared by first ball milling an ethanol-dispersed mixture of MnOₓ xerogel or aerogel with XC-72 and PFTE polymer binder in a mass ratio of 20/65/15 for 16 h using a U.S. Stoneware Jar Mill with zirconia milling media at a variable speed of 200 rpm. A 1/2” nickel mesh was then sandwiched between the nickel flag aligned in the middle. The electrolyte reserve was filled with 6 M KOH and the positive terminal lead. Voltage–capacity trends were measured using a Fisher Scientific AB15 pH meter. The counter electrode used for these measurements was a gold mesh and the positive terminal lead. Voltage–capacity trends were measured at constant-current densities spanning 5–125 mA cm⁻² and discharging to capacities that sum to a total depth of discharge of 20% of the theoretical capacity of zinc (819.73 mAh g⁻¹ Zn), highlighting the stability of the ORR response in continuous-operation mode, as opposed to short-duration pulses that are sometimes used for reports on air-cathode performance.

Results and Discussion

Materials characterization.—The structural characteristics of the MnOₓ xerogels and aerogels were first determined prior to electrochemical testing. The MnOₓ xerogel and aerogel nanoarchitectures exhibit the cryptomelane 2 × 2 × 2 tunnel structure as verified by X-ray diffraction (α-MnO₂; ICDD #00-044-1386; crystal structure is shown in the inset of Figure 1a). The broad X-ray reflections indicate nanoscale features; Scherrer analysis yields average crystallite sizes of ~7 nm in both cases. Prior transmission electron microscopy of related cryptomelane-MnOₓ nanoarchitectures showed a nanorod-like morphology, ~5 nm wide by 10–30 nm long. When examined by field-emission scanning electron microscopy (SEM), xerogels present a more dense structure of networked MnOₓ nanoparticles (Figure 1b), whereas the corresponding aerogel has a highly textured, ultra porous structure (Figure 1c). Nitrogen-sorption analysis (nitrogen-sorption porosimetry isotherms and pore size distributions of MnOₓ xerogel and aerogel can be found in Figures S1a,b) reveals that both calcined MnOₓ forms exhibit high specific surface area, though the aerogel is superior at 181 m² g⁻¹ vs. 137 m² g⁻¹ for the xerogel (Table I). Xerogel and aerogel forms are further differentiated by their total pore volume, which is 0.6 cm³ g⁻¹ for the xerogel and aero-gel and a total of 7 nm in both cases. Prior transmission electron microscopy of related cryptomelane-MnOₓ nanoarchitectures showed a nanorod-like morphology, ~5 nm wide by 10–30 nm long. When examined by field-emission scanning electron microscopy (SEM), xerogels present a more dense structure of networked MnOₓ nanoparticles (Figure 1b), whereas the corresponding aerogel has a highly textured, ultra porous structure (Figure 1c). Nitrogen-sorption analysis (nitrogen-sorption porosimetry isotherms and pore size distributions of MnOₓ xerogel and aerogel can be found in Figures S1a,b) reveals that both calcined MnOₓ forms exhibit high specific surface area, though the aerogel is superior at 181 m² g⁻¹ vs. 137 m² g⁻¹ for the xerogel (Table I). Xerogel and aerogel forms are further differentiated by their total pore volume, which is 0.6 cm³ g⁻¹ for the low-density aerogel compared to 0.6 cm³ g⁻¹ for the xerogel.

Electroanalytical assessment at rotating-disk electrodes.—The fundamental oxygen-reduction activity of the MnOₓ xerogel and aerogel was assessed at RDEs (Figure 2a), a common method used to screen MnOₓ electrocatalysts. Linear–wave voltammograms of ink–cast carbon + MnOₓ films at glassy-carbon RDEs in O₂-saturated 1 M KOH show the characteristic sigmoidal shape for O₂ reduction, with comparable onset potential of 0.9 V vs. RHE, which translates to an overpotential of η ≈ 310 mV (complementary plots referenced to Hg/HgO and overpotentials are shown in Figure S2). Previous studies on tanned α-MnO₂ reported similar values of onset potential and limiting current density. The effectiveness of manganese oxides as alkaline ORR catalysts is further confirmed here, with onset potentials that are only ~70 mV more negative than for carbon-supported Pt nanoparticles.

These RDEs were subjected to a range of rotation rates (ω), with the resulting trends in current density values (J) used to calculate the number of electrons passed (nₑ), according to the Rountell–Levich theory:

\[ \begin{align*}
J / \omega & = 1 / J_0 + 1 / J_f = 1 / B \omega^{1/2} + 1 / J_k \end{align*} \quad [2] \]
where $J_K$ is the kinetics-limited current density ($J_K = n_e F k C_O$), and $J_L$ is the diffusion-limited current density. The $B$ term is further defined as:

$$B = 0.62 n_e F C_O (D_O)^{2/3} \nu^{-1/6}$$  \hspace{1cm} [3]$$

where $F$ is the Faraday constant (96,485 C mol$^{-1}$), $C_O$ is the bulk concentration of O$_2$ ($7.8 \times 10^{-7}$ mol cm$^{-3}$), $D_O$ is the diffusion coefficient of O$_2$ ($1.8 \times 10^{-5}$ cm$^2$ s$^{-1}$), and $\nu$ is the kinematic viscosity of 1 M KOH (0.01 cm$^2$ s$^{-1}$). Values of $B$ were derived from the slopes of plots of inverse current density vs. the inverse square of rotational speed ($\omega^{-1/2}$) (Figure S3a and Figure S3b for xerogel and aerogel, respectively). For both of the MnO$_x$ nanoarchitectures, we determined $n_e = 4$ (Table II), indicating a four-electron pathway for reducing O$_2$ to OH$^-$.

This value is consistent with that reported for 1D tunneled $\alpha$-MnO$_2$ electrocatalysts. While beyond the scope of this
Table I. Summary of physical properties of MnO\textsubscript{x} xerogels and aerogels.

| MnO\textsubscript{x} form | Average crystallite size (nm)\textsuperscript{a} | Specific surface area (m\textsuperscript{2} g\textsuperscript{−1}) | BJH pore volume (cm\textsuperscript{3} g\textsuperscript{−1}) |
|--------------------------|-----------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Xerogel                  | 7                                             | 137                                             | 0.6                                             |
| Aerogel                  | 7                                             | 181                                             | 1.5                                             |

\textsuperscript{a}Crystallite sizes were calculated from the full-width at half-maximum of all the prominent peaks from 20–70° 2θ (See Fig 1a) using the Scherrer equation; the values were then averaged.

In order to fabricate practical composite electrode structures for this study, MnO\textsubscript{x} xerogel and aerogel powders were first ball-milled with Vulcan carbon powder and PTFE binder; a Ni-mesh current collector was then sandwiched between the MnO\textsubscript{x}/carbon/PTFE mixtures by pressing at 1750 psi. The resulting electrodes were interfaced with an air-breathing electroanalytical cell (Figure 3a),\textsuperscript{25} with one side contacting a battery-relevant electrolyte (aqueous 6 M KOH) and the other side exposed to static air. Electrocatalytic activity for ORR was assessed with potential-step chronoamperometry within a potential window of 1.4 to 0.9 V vs. Zn/Zn\textsuperscript{2+}, a range typical of a zinc–air cell. Potential-dependent steady-state current density trends obtained with the MnO\textsubscript{x} xerogel and aerogel–containing composite electrodes are shown in Figure 4b from 1.4 to 1.1 V.

The ORR performance of MnO\textsubscript{x} xerogel and aerogel immediately begins to diverge as the potential is stepped down from 1.40 V to 1.35 V and below. For example, at 1.35 V the aerogel-based electrode provides a current density of –20 mA cm\textsuperscript{−2}, while the xerogel-based analog yields only –7 mA cm\textsuperscript{−2}. To match the –20 mA cm\textsuperscript{−2} activity of the aerogel at 1.35 V, the xerogel must operate at 1.28 V, a 70-mV penalty in overpotential (Table II).

The performance of the MnO\textsubscript{x} xerogel-based electrode is consistent with that previously reported for powder composites incorporating nanoscale α-MnO\textsubscript{2} as the active catalyst, for example the work of Cao et al.\textsuperscript{6} The enhanced performance of the aerogel-based air cathode at

Table II. Summary of electrochemical properties of MnO\textsubscript{x} xerogels and aerogels.

| MnO\textsubscript{x} form | ORR \( n_e \)\textsuperscript{4} | Onset overpotential (mV)\textsuperscript{b} | Potential at –20 mA cm\textsuperscript{−2} (V vs. Zn/Zn\textsuperscript{2+})\textsuperscript{b} | Potential at –40 mA cm\textsuperscript{−2} (V vs. Zn/Zn\textsuperscript{2+})\textsuperscript{b} | Discharge Voltage at –25 mA cm\textsuperscript{−2} (V)\textsuperscript{c} | Discharge Voltage at –125 mA cm\textsuperscript{−2} (V)\textsuperscript{c} |
|--------------------------|-------------------------------|---------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Xerogel                  | 3.94 ± 0.05                   | 310                                         | 1.28                                            | 1.23                                            | 1.05                                            | 0.83                                            |
| Aerogel                  | 4.00 ± 0.02                   | 310                                         | 1.35                                            | 1.28                                            | 1.2                                             | 0.93                                            |

\textsuperscript{a}Electrochemical measurements assessed at half-cell glassy-carbon rotating disk electrodes.

\textsuperscript{b}Electrochemical measurements performed using an air-breathing half-cell configuration.

\textsuperscript{c}Electrochemical performance determined using full-cell zinc–air cells paired with a 3D zinc sponge anode.

Figure 3. (a) Schematic of the air-breathing electroanalytical cell (adapted from Fig. 1 in Ref. 25); (b) Current–potential response over the oxygen-reduction potential window (1.1–1.4 V vs. Zn/Zn\textsuperscript{2+}) in 6 M KOH under static air for MnO\textsubscript{x} xerogel and aerogel.
Figure 4. (a) Schematic of a zinc–air cell using a nylon button-cell configuration. (b) Voltage–capacity trends reported at sustained current densities of 5, 10, 25, 50, 100, and 125 mA cm$^{-2}$.

Figure 5. Field-emission scanning electron micrographs of the top surface of MnOx-based powder composites: (a) xerogel and (b) aerogel. Scanning electron micrograph and energy-dispersive spectroscopic chemical mapping for C, O, and Mn of MnOx-based powder composites: (c) xerogel and (d) aerogel.
moderate overpotentials may arise from improved short-range transport of O2 to catalytically active sites at the oxide surface, facilitated by the aerogel’s high pore volume37 and hierarchical dispersity of pore size.

Zinc–air full cell performance evaluation.— Two-terminal zinc–air full cells were assembled to validate the distinctions observed between the MnOx xerogel and aerogel carbon–composite electrodes in the air-breathing half-cell, but now, under technologically relevant, limited-electrolyte conditions. Zinc sponge electrodes, recently developed in our laboratory, were chosen for full-cell demonstrations, because the interconnecting, co-continuous networks of solid metal and electrolyte-filled void in the sponge confer higher capacity and rates relative to commercial, powder-bed counterparts;26,27,38 thus, the sponge electrode form-factor is less likely to limit performance at the opposing air cathode. Galvanostatic discharge measurements were applied to the resulting button cells, with current densities ranging from 5–125 mA cm–2 to monitor the ability of the zinc–air full cell to sustain steady-state discharge voltages at these moderate to challenging rates.

At moderate rates (5–50 mA cm–2), the MnOx aerogel carbon–composite electrode confers higher discharge voltages than its xerogel counterpart (by ~60 mV; Figure 4). At more challenging rates (>50 mA cm–2), the separation in discharge voltage expands to ~100 mV (Table II). By 125 mA cm–2, the discharge voltage of the xerogel-based cell falls below the conventional lower voltage limit used for zinc–air cells (0.90 V),39 whereas the aerogel analog maintains voltage at 0.93 V, within practical operating conditions. The maximum specific power observed for the MnOx aerogel-based zinc–air cell, normalized to the mass of the zinc electrode, is 1,250 W kgZn–1. Projecting this value to a fully packaged cell where zinc commonly occupies 46% of the battery40 translates to a specific power of 580 W kg–1 and a corresponding area-normalized power of 112 mW cm–2. The discharge voltage and area-normalized power with xerogel-based electrodes are commensurate with other device-level zinc–air cells using MnOx-type catalysts,41–44 while MnOx aerogel–based air cathodes boost the ORR performance beyond typical.

With aerogel-based composite electrodes providing clear performance advantages, we turned to SEM and EDS to characterize the nano- and micro-scale structure of the composite electrodes. In both cases, micrographs show a well-dispersed matrix containing all three components—nanofibers of PTFE interspersed among agglomerates of ~50-nm carbon particles and nanostructured MnOx (Figures 5a, 5b)—with no obvious micrographic distinctions between aerogel- and xerogel-based powder–composites. We used EDS in elemental mapping mode to examine for Mn- and O-containing domains that would be associated with the MnOx phase (Figures 5c, 5d). When the xerogel powder–composite is imaged in multiple locations on the composite surface (Figures S5 and S6 for xerogel and aerogel, respectively), the Mn and O EDS maps show that localized MnOx rich features are observed in the elemental map of the aerogel-based powder–composite (Figures 5d), which exhibits more homogeneous Mn and O distribution at this size scale.

To probe the internal structure of these powder composites, cross sections of both xerogel and aerogel powder–composite electrodes were prepared by Ga+ ion-beam milling and imaged by SEM (Figures 6a, 6b). The bright spots in the moderate-magnification SEM indicate a few zirconia particles introduced during the ballmilling process; XPS analysis shows that zirconium content is less than 1% (see Supporting Information). At finer magnification, the aerogel-based composite shows markedly higher void space compared to the xerogel (Figures 6c, 6d), which correlates with the results of the
nitrogen-sorption porosimetry data presented in Table I for the MnOx aerogel itself. Elemental mapping of the cross-sections yields similar results to those obtained at the outer surface, with the xerogel-based composite showing evidence of some inhomogeneities (regions with high Mn and O concentration). On the basis of the SEM/EDS results, we posit that the low density and friable nature of the MnOx aerogel yields a more uniform dispersion within the carbon/PTFE matrix during the ballmilling process, which leads to enhanced ORR activity in a technologically relevant electrode structure.

Conclusions

The results reported herein highlight the importance of assessing the translation of electrocatalytic activity from fundamental measurements to technologically relevant electrode structures. Fundamental studies derived from rotating-disk electrodes yield key information such as electrocatalytic mechanisms, yet do not provide insight into overall catalytic activity when expressed in a microheterogeneous structure that includes conductive carbon and polymer binder. Configurations that test powder-composite electrodes in an air-breathing mode show clear distinctions in ORR activity for xerogel versus aerogel-based compositions, and the performance evaluation is a better predictor of real full cell performance than the fundamental RDE study. The performance trends reported in this study—lower overpotentials and higher discharge voltages for MnOx aerogel-based composite electrodes—presents an exciting direction for establishing device-relevant metrics of ORR catalyst materials.

Acknowledgments

The authors acknowledge the financial support from the U.S. Office of Naval Research. J.S.K. is an NRL-NRC Postdoctoral Associate (2016–Present). M.N.V. was a Naval Research Enterprise Internship Program (NREIP) undergraduate research student (2016–2017).

References

1. K. A. Stoerzinger, M. Risch, B. Han, and Y. Shao-Horn, *ACS Catal.*, 5, 6021 (2015).
2. Y. Meng, W. Song, H. Huang, Z. Ren, S.-Y. Chen, and S. L. Suib, *J. Am. Ceram. Soc.*, 93, 11452 (2014).
3. V. Neburchilov, H. Wang, J. J. Martin, and W. Qiu, *J. Power Sources*, 195, 1271 (2010).
4. F. Cheng, Y. Su, J. Liang, Z. Tao, and J. Chen, *Chem. Mater.*, 22, 898 (2010).
5. L. Mao, T. Sotomura, K. Nakatsu, N. Koshiba, D. Zhang, and T. Ohsaka, *J. Electrochem. Soc.*, 149, A504 (2002).
6. Y. L. Cao, H. X. Yang, X. P. Ai, and L. F. Xiao, *J. Electroanal. Chem.*, 557, 127 (2003).
7. A. S. Ryabova, N. شامله F, T. Poue, S. Y. Iotomin, A. Bonnefont, D. M. Antipin, A. Y. Baranchikov, E. L. Levin, A. M. Abakumov, G. Kéranov, E. V. Antipov, G. A. Tsirlina, and E. R. Savinova, *Electrochim. Acta*, 187, 161 (2016).
8. E. M. Benbow, S. P. Kelly, L. Zhao, J. W. Reustenauer, and S. L. Suib, *J. Phys. Chem. C*, 115, 22009 (2011).
9. W. Xiao, D. Wang, and X. W. Lou, *J. Phys. Chem. C*, 114, 1694 (2010).
10. A. R. Mainur, L. C. Colmenares, O. Leonet, F. Alcaide, J. J. Irvin, S. Weinberger, V. Hacker, E. Irwin, I. Urdanpilleta, and J. Alberto Blazquez, *Electrochim. Acta*, 217, 80 (2016).
11. X. Zheng, L. Yu, B. Lan, G. Cheng, T. Lin, B. He, W. Ye, M. Sun, and F. Ye, *J. Power Sources*, 362, 332 (2017).
12. Q. Tang, L. Jiang, J. Liu, S. Wang, and G. Sun, *ACS Catal.*, 4, 457 (2014).
13. B. Klášťové, J. Vondráek, and J. Velická, *Electrochim. Acta*, 47, 2365 (2002).
14. A. Loh, K. Xu, X. Li, and B. Wang, *Electrochim. Acta*, 245, 615 (2017).
15. J.-S. Lee, G. S. Park, H. I. Lee, S. T. Kim, R. Cao, M. Liu, and J. Cho, *Nano Lett.*, 11, 5362 (2011).
16. H.-Y. Park, T. J. Shin, H.-I. Joo, J. H. Jang, D. Ahn, and S. J. Yoo, *Electrochem. Commun.*, 41, 35 (2014).
17. C. N. Chernov, J. W. Long, N. L. Brandell, J. M. Wallace, N. W. Kucko, and D. R. Rolison, *J. Power Sources*, 207, 191 (2012).
18. M. C. Wu, T. S. Zhao, H. R. Jiang, L. Wei, and Z. H. Zhang, *Electrochim. Acta*, 222, 1438 (2016).
19. A. S. Ryabova, A. Bonnefont, P. A. Simonov, T. Dintzer, C. Ulhaq-Bouillet, Y. G. Bogdanova, G. A. Tsirlina, and E. R. Savinova, *Electrochim. Acta*, 246, 643 (2017).
20. Q. Yu, J. Xu, C. Wu, J. Zhang, and L. Guan, *ACS Appl. Mater. Interfaces*, 8, 35264 (2016).
21. J. W. Long, K. E. Swider-Lyons, R. M. Stoud, and D. R. Rolison, *ECS Solid State Lett.*, 3, 453 (2000).
22. C. N. Chernov, P. A. DeSario, J. F. Parker, E. S. Nelson, B. W. Miller, D. R. Rolison, and J. W. Long, *ChemElectroChem*, 3, 1369 (2016).
23. J. S. Ko, C. N. Chernov, M. N. Vila, P. A. DeSario, J. F. Parker, J. W. Long, and D. R. Rolison, *Langmuir*, 33, 9390 (2017).
24. M. W. Louis and A. T. Bell, *J. Am. Chem. Soc.*, 135, 12329 (2013).
25. C. N. Chernov, J. F. Parker, E. S. Nelson, D. R. Rolison, and J. W. Long, *Nanotechnology*, 27, 174002 (2016).
26. J. F. Parker, C. N. Chernov, E. S. Nelson, D. R. Rolison, and J. W. Long, *Energy Environ. Sci.*, 7, 1117 (2014).
27. J. F. Parker, E. S. Nelson, M. D. Wattendorf, C. N. Chernov, J. W. Long, and D. R. Rolison, *ACS Appl. Mater. Interfaces*, 6, 19471 (2014).
28. B. Pommack and J. R. Dahn, *J. Electrochem. Soc.*, 159, A981 (2012).
29. D. E. Turney, J. W. Gallaway, G. G. Yadav, R. Ramirez, M. Nyce, S. Banerjee, Y. K. Chen-Wiegart, J. Wang, M. J. D’Ambrose, S. Kolhekar, J. Huang, and X. Wei, *Chem. Mater.*, 29, 4819 (2018).
30. L. Geniès, R. Faure, and R. Durand, *Electrochim. Acta*, 44, 1317 (1998).
31. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed. (John Wiley & Sons, 2001), pp. 471.
32. J. Qiao, L. Xu, L. Ding, P. Shi, L. Zhang, R. Baker, and J. Zhang, *Int. J. Electrochem. Sci.*, 8, 1189 (2013).
33. R. Zhou, Y. Zheng, M. Jaroniec, and S.-Z. Qiao, *ACS Catal.*, 6, 4720 (2016).
34. Y. Garsany, O. A. Baturina, S. S. Kocha, and K. E. Swider-Lyons, *Anal. Chem.*, 82, 6321 (2010).
35. Y. Huang, Y. Lin, and W. Li, *Electrochim. Acta*, 99, 161 (2013).
36. P.-O. Li, C.-C. Hu, H. Noda, and H. Habazaki, *J. Power Sources*, 298, 102 (2015).
37. D. R. Rolison, *Science*, 299, 1698 (2003).
38. J. F. Parker, C. N. Chernov, I. R. Pala, M. Machler, M. F. Burz, J. W. Long, and D. R. Rolison, *Science*, 356, 415 (2017).
39. D. Linden, *Handbook of Batteries*, 2nd ed. (McGraw-Hill, 1995), pp. 13.1.
40. Primary Zinc Air Button Cell Batteries Product Safety Data Sheet. 17 April 2010, https://sep.yimg.com/vt/cto/theshorelmenemarket/Duracell-Zinc-Air-Batteries-North-America-MSDS.pdf?&t=1509744871&. 41. G. Q. Zhang and X. G. Zhang, *Electrochim. Acta*, 49, 873 (2004).
42. G.-Q. Zhang, X.-G. Zhang, and H.-L. Lin, *J. Solid State Electr.*, 10, 995 (2006).
43. H. Ma, B. Wang, Y. Fan, and W. Hong, *Energy*, 7, 6549 (2014).
44. M. Xiong and D. G. Ivey, *J. Electrochem. Soc.*, 164, A1012 (2017).