Electrocatalytic Measurement Methodology of Oxide Catalysts Using a Thin-Film Rotating Disk Electrode

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<td><strong>As Published</strong></td>
<td><a href="http://dx.doi.org/10.1149/1.3456630">http://dx.doi.org/10.1149/1.3456630</a></td>
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<tr>
<td><strong>Publisher</strong></td>
<td>The Electrochemical Society</td>
</tr>
<tr>
<td><strong>Version</strong></td>
<td>Final published version</td>
</tr>
<tr>
<td><strong>Citable link</strong></td>
<td><a href="http://hdl.handle.net/1721.1/79061">http://hdl.handle.net/1721.1/79061</a></td>
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Transition-metal oxides can exhibit high electrocatalytic activity for reactions such as the oxygen reduction reaction (ORR) in alkaline media. It is often difficult to measure and compare the activities of oxide catalysts on either per square area basis, because of the poorly defined oxygen transport to and within porous oxide electrodes of several tens of micrometers thickness. A more systematic evaluation of the ORR activities of submicrometer-sized transition-metal oxides. Thin films of LaNiO₃, LaCu₀.₅Mn₀.₅O₃, and La₀.₇₅Ca₀.₂₅FeO₃ oxide particles were bonded to glassy carbon via an ion-exchanged Nafion binder, and their mass and specific ORR activities were extracted from rotating disk electrode measurements. We found that the specific activity of LaNiO₃ was much higher than that of La₀.₇₅Ca₀.₂₅FeO₃ and LaCu₀.₅Mn₀.₅O₃. The projection of LaNiO₃ in the actual fuel cell cathode was presented, which was shown to be competitive with current platinum-based cathodes.

Experimental

Synthesis and characterization.— The perovskite transition-metal oxides studied in this paper (La₀.₇₅Ca₀.₂₅FeO₃, LaCu₀.₅Mn₀.₅O₃, and LaNiO₃) represent the full ORR activity range obtained for various oxides measured in our laboratory, which were synthesized using a co-precipitation method described elsewhere. Briefly, rare-earth and alkali-earth nitrates and transition-metal nitrates (all 99.98% purity, Alfa Aesar), at the respective stoichiometric ratio, were mixed in Milli-Q water (18 MΩ cm) at metal concentrations on the order of 0.1 M. This solution was then titrated with 1.2 M tetramethylammonium hydroxide (Alfa Aesar) until a solid precipitate was formed. The precipitate was filtered, collected, and dried at 200 °C for 12 h, and then subjected to heat-treatment at 1000 °C in dry air (ultrahigh purity grade, Airgas) for 12 h for La₀.₇₅Ca₀.₂₅FeO₃ and LaCu₀.₅Mn₀.₅O₃. To ensure the oxygen stoichiometry of LaNiO₃, this sample was synthesized at 800 °C in pure O₂ (ultrahigh purity grade, Airgas) for 8 h, and thermogravimetric analysis (Perkin-Elmer) was used to confirm that its oxygen content was approximately 98% of the nominal value. X-ray diffraction

Manuscript submitted March 18, 2010; revised manuscript received May 10, 2010. Published July 7, 2010.

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Nafion, 29 was made by adding a defined aliquot of 0.1 M NaOH to sodium hydroxide which, similar to an earlier report on lithiated \( \text{H}_2 \text{O}_8 \) the catalyst surface. To avoid possible corrosion of the oxide due to particles determined by scanning electron microscopy believed that a comparison of the specific ORR activity of the various oxides on GC disk for thin-film RDE measurements with perovskite samples in this work are hundreds of nanometer in size, ovskite samples in this work are hundreds of nanometer in size, \( \text{Fe}_3 \text{O}_4 \) for nonsupported oxide catalysts can also be determined from nitro-
mass specific surface areas \( \sigma \) is the volume/area averaged diameter. 28 While the value of \( s \) is the oxide bulk density, \( d \) is the diameter of individual particles determined by scanning electron microscopy (SEM), and \( d_{av} \) is the volume/area averaged diameter. 29 While the value of \( A_s \) for nonsupported oxide catalysts can also be determined from nitrogen Brunauer, Emmett, and Teller (BET) area measurements, we did not have sufficient material for most of our samples to conduct meaningful BET analysis. Sufficient material for BET analysis was only available for LaNiO_3, and the measured BET area of \( \approx 5.6 \text{ m}^2 \text{ g}^{-1} \) (Micromeritics ASAP2040) was reasonably consistent with the SEM-based value of \( \approx 3.5 \text{ m}^2 \text{ g}^{-1} \). Therefore, it is believed that a comparison of the specific ORR activity of the various oxides using the SEM-based \( A_s \)-values listed in Table I is reasonably accurate.

**Ion-exchanged Nafion solution preparation.** — Because the perovskite samples in this work are hundreds of nanometer in size, oxide coatings on GC disk for thin-film RDE measurements with these relatively large and heavy catalyst particles require an immobilizing binder that also facilitates the transport of dissolved \( \text{O}_2 \) to the catalyst surface. To avoid possible corrosion of the oxide due to the strong acidity of commercially available Nafion solution (DE520, Ion Power, DE), we ion-exchanged the solution with sodium hydroxide which, similar to an earlier report on lithiated Nafion, 29 was made by adding a defined aliquot of 0.1 M NaOH to the Nafion solution: For an equivalent weight of \( \text{Na}^+ \)-exchanged Nafion solution with tetrahydrofuran (THF, 99.9 \% Sigma-Aldrich), yielding inks with final concentrations of \( 5 \text{ m}_{\text{oxide}} \text{ mL}_{\text{ink}}^{-1} \), \( 1 \text{ mg}_{\text{AB}} \text{ mL}_{\text{ink}}^{-1} \), and \( 1 \text{ mg}_{\text{Nafion}} \text{ mL}_{\text{ink}}^{-1} \). Next, \( 10 \mu \text{L} \) of catalyst ink was drop-cast onto a GC electrode (0.196 \text{ cm}^2 area, Pine, NC) polished to a mirror finish with 0.05 \mu \text{m} alumina slurry (Buehler). The catalyst layer on the GC substrate was dried overnight in a sealed glass jar that had been presaturated with THF vapor, enabling slow ink drying rates which were found to be required for homogeneous thin-film coatings on the GC disk electrode. The electrode had a final composition of \( 250 \mu \text{ g}_{\text{oxide}} \text{ cm}_{\text{disk}}^{-1} \), \( 50 \mu \text{ g}_{\text{AB}} \text{ cm}_{\text{disk}}^{-1} \), and \( 50 \mu \text{ g}_{\text{Nafion}} \text{ cm}_{\text{disk}}^{-1} \) at an estimated film thickness of \( \approx 2 \mu \text{m} \). Based on the density of water-immersed-reconstituted Nafion of \( \approx 1.4 \text{ g cm}^{-3} \), the Nafion film thickness based on the geometric area of the disk would correspond to \( \approx 0.4 \mu \text{m} \), which is sufficiently thin so that \( \text{O}_2 \) transport resistance within the ionomer phase is negligible. 34 Assuming uniform Nafion coverage on oxide and carbon particles in the electrodes, we found that the actual Nafion film thickness is more than 1 order of magnitude lower because of the high electrode roughness factors of oxide and carbon of \( \approx 2.5 \text{ cm}_{\text{oxide}} \text{ cm}_{\text{disk}}^{-1} \), \( 30 \mu \text{ g}_{\text{AB}} \text{ cm}_{\text{disk}}^{-1} \), and \( 25 \mu \text{ g}_{\text{Nafion}} \text{ cm}_{\text{disk}}^{-1} \). The Pt/C surface area was estimated from the electrochemical \( \text{H}_2 \) underpotential deposition, as described elsewhere, 34, 35 and yielded a Pt specific surface area of 48 \text{ m}^2 \text{ g}^{-1}.

**Platinum electrode preparation.** — GC disk electrodes coated with a thin film of Pt/C catalyst (46 wt \% Pt on high surface area carbon, Tanaka Kikinzoku Kogyo, Japan) were prepared as described elsewhere. 3 Briefly, 15 \mu \text{L} of an aqueous Pt/C ink, composed of 0.15 mg_{\text{Pt}} mL^{-1} and 0.04 mg_{\text{Nafion}} mL^{-1}, was drop-cast onto a GC disk electrode and allowed to dry overnight, yielding a Pt loading of \( 5 \mu \text{g}_{\text{Pt}} \text{ cm}_{\text{disk}}^{-1} \) and \( 3 \mu \text{g}_{\text{Nafion}} \text{ cm}_{\text{disk}}^{-1} \). The Pt/C surface area was estimated from the electrochemical \( \text{H}_2 \) underpotential deposition, as described elsewhere, 34, 35 and yielded a Pt specific surface area of 48 \text{ m}^2 \text{ g}^{-1}.

**Electrochemical characterization.** — All electrochemical measurements were conducted in a three-electrode glass cell (Pine Instrument, and using a rotator (Pine) to which the thin-film RDE working electrodes were attached; the potential was controlled using a VoltaLab PST050 potentiostat. The 0.1 M KOH electrolyte was prepared from Milli-Q water (18 \text{ M}\Omega cm) and KOH pellets (99.99\% purity, Sigma-Aldrich). All measurements were conducted at 10 mV s^{-1} in either \( \text{N}_2 \) or \( \text{O}_2 \) (ultrahigh purity grade, Airgas) at room temperature. A saturated calomel electrode as reference electrode (Pine Instrument) was used and calibrated in the same electrolyte by measuring hydrogen oxidation/evolution currents on Pt-RDE and defining the potential of zero current as the reversible hydrogen electrode (RHE) potential. In this case, 0 V vs RHE corresponds to 0.998 \pm 0.005 V vs RHE. All the potentials in this study were referenced to the RHE potential scale and correspond to the applied potentials, \( E_{\text{applied}} \) unless they are stated to be iR-corrected potentials, \( E_{\text{iR-corrected}} \) calculated by the following equation

**Table I. SEM characterization of the oxides studied in this work.**

<table>
<thead>
<tr>
<th>Space group</th>
<th>( d_{av} ) (\mu m)</th>
<th>( d_m ) (\mu m)</th>
<th>( A_s ) (m( ^2 ) g(^{-1} ))</th>
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<tr>
<td>LaNiO(_3)</td>
<td>( R\overline{3}c )</td>
<td>0.20 (\pm 0.06)</td>
<td>0.24</td>
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<tr>
<td>La(<em>{0.5})Ca(</em>{0.5})Mn(_{0.5})O(_3)</td>
<td>( P\overline{mmm} )</td>
<td>0.58 (\pm 0.28)</td>
<td>0.80</td>
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<tr>
<td>La(<em>{0.5})Ca(</em>{0.25})Fe(_3)O(_5)</td>
<td>( R\overline{3}c )</td>
<td>0.36 (\pm 0.22)</td>
<td>0.59</td>
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Figure 1. (Color online) XRD spectra of the oxides studied in this work.
Mass-transport-corrected kinetic ORR current density, and O₂-saturated 0.1 M KOH. ORR activities were obtained from the 0.1 M KOH at room temperature in N₂-saturated electrolyte at 0 rpm (blue) or in O₂-saturated electrolyte at 1600 rpm. Sweep directions are shown by the arrow.

\[
E_{\text{IR-corrected}} = E_{\text{applied}} - iR
\]

where \( i \) is the current and \( R \) is the uncompensated ohmic electrolyte resistance (=45 Ω) measured via high frequency ac impedance in O₂-saturated 0.1 M KOH. ORR activities were obtained from the negative-going scans in pure O₂ at 1600 rpm and were corrected for capacitive currents in pure N₂. Error bars represent standard deviations from at least three independent repeated measurements, whereby the change in activity over subsequent potential cycles is less than 3%. To achieve this steady-state response, the potential range was kept within 0.7–1 V vs RHE to prevent degradation of the oxide catalysts by oxidation/reduction; in addition, the ORR activity below 0.7 V could not be quantified in any case due to the interference from the carbon added to the electrode. ORR data at lower potentials are only shown for LaCu₀.₅Mn₀.₅O₃, which displayed remarkable stability down to 0.4 V vs RHE, and for Pt in negative-going scans in pure O₂ at 1600 rpm and were corrected for capacitive currents in pure N₂.

The mass transport correction was performed using the well-known Levich equation:

\[
i_{\text{measured}} = i_{\text{k}} + i_{\text{d}}
\]

where \( i_{\text{measured}} \) is the measured O₂ reduction current density, \( i_{\text{k}} \) is the mass-transport-corrected kinetic ORR current density, and \( i_{\text{d}} \) represents the limiting current density, which was obtained experimentally for LaNiO₃ and LaCu₀.₅Mn₀.₅O₃ electrodes (vide infra).

To avoid impurities from the corrosion of the glass cell, all experiments were collected within 2 h of the initial exposure of KOH to the glass cell. The absence of contamination effects from the glass cell under these conditions is demonstrated by the fact that the ORR mass activity at 0.9 V vs RHE of Pt/C obtained in our glass cell under these conditions is demonstrated by the fact that reported for a Teflon cell, confirming the high ORR activity of LaNiO₃. Figure 3 compares the ORR activity of LaCu₀.₅Mn₀.₅O₃ with this work, showing the capacity-corrected net ORR current densities of the negative-going scan at a rotation rate of 1600 rpm. The ORR activity of the GC substrate and AB added to oxide electrodes is also shown in Fig. 3, indicating that background contributions from the AB and GC disk are negligible above ~0.7 V vs RHE. Therefore, even for the oxide with the lowest measured ORR activity (La₀.₇₅Ca₀.₂₅FeO₃), the background contribution from carbon materials is negligible, and the measured ORR activity is that of the oxide itself. The more than 0.22 V lower ORR activity of La₀.₇₅Ca₀.₂₅FeO₃ compared with LaNiO₃ (Fig. 3) is somewhat surprising because similar exchange current densities were reported previously for LaNiO₃, La₀.₇Sr₀.₃FeO₃, and La₀.₅Sr₀.₅FeO₃, and because one would not expect that the exchange of A-site atoms of different sizes (i.e., Sr for Ca) would produce such a large shift in ORR activity (e.g., the ORR activity of AMnO₃ compounds is within 50 mV for A = La, Pr, Nd, Sm, Gd, Dy, or Y[15]). This discrepancy may be related to the strong O₂ mass transport limitations in thick, high porosity pellet electrodes used previously, rendering the quantification of the ORR activity ambiguous, if not impossible, and highlighting the need for a simple ORR activity measurement method with well-controlled O₂ mass transport properties.

Figure 4 compares the ORR activity of LaCu₀.₅Mn₀.₅O₃ with

\[
E_{\text{hours}} = 0.45 \Omega
\]

La₂₀₃ has been known as a highly active ORR catalyst for some time[16,39] and was recently applied as a cathode catalyst in a sodium-borohydride/air fuel cell. Figure 2 shows the cyclic voltammogram of a thin-film LaNiO₃ electrode in N₂-saturated 0.1 M KOH at 10 mV s⁻¹, indicating the absence of any noticeable oxidation/reduction feature in the range of 0.7–1.0 V RHE, consistent with previous reports. Most ORR activity studies in the past use a Hg/HgO reference scale, whereby 0 V RHE corresponds to approximately ~0.92 V Hg/HgO. In O₂-saturated 0.1 M KOH, the onset of ORR currents is observed below ~0.95 V vs RHE (see Fig. 2), confirming the high ORR activity of LaNiO₃. Figure 3 compares the ORR activity of three different perovskites examined in this work, showing the capacity-corrected net ORR current densities of the negative-going scan at a rotation rate of 1600 rpm. The ORR activity of the GC substrate and AB added to oxide electrodes is also shown in Fig. 3, indicating that background contributions from the AB and GC disk are negligible above ~0.7 V vs RHE. Therefore, even for the oxide with the lowest measured ORR activity (La₀.₇₅Ca₀.₂₅FeO₃), the background contribution from carbon materials is negligible, and the measured ORR activity is that of the oxide itself. The more than 0.22 V lower ORR activity of La₀.₇₅Ca₀.₂₅FeO₃ compared with LaNiO₃ (Fig. 3) is somewhat surprising because similar exchange current densities were reported previously for LaNiO₃, La₀.₇Sr₀.₃FeO₃, and La₀.₅Sr₀.₅FeO₃, and because one would not expect that the exchange of A-site atoms of different sizes (i.e., Sr for Ca) would produce such a large shift in ORR activity (e.g., the ORR activity of AMnO₃ compounds is within 50 mV for A = La, Pr, Nd, Sm, Gd, Dy, or Y[15]). This discrepancy may be related to the strong O₂ mass transport limitations in thick, high porosity pellet electrodes used previously, rendering the quantification of the ORR activity ambiguous, if not impossible, and highlighting the need for a simple ORR activity measurement method with well-controlled O₂ mass transport properties.

Figure 4 compares the ORR activity of LaCu₀.₅Mn₀.₅O₃ with
Pt/C at 1600 rpm and 10 mV s$^{-1}$, showing that the same diffusion-limited current density of $\sim$5.7 mA cm$^{-2}$ was obtained for both catalysts. This value is consistent with the 4-electron limiting current for $O_2$ reduction to water, which has been reported previously for platinum single crystal and polycrystalline electrodes in 0.1 M KOH at room temperature. Therefore, one can conclude that $O_2$ is reduced to water in an overall 4-electron process on the thin-film LaCu$_{0.5}$Mn$_{0.5}$O$_3$ electrode, which was also confirmed by the Koutecky–Levich analysis shown in Fig. 5, where the slope of the lines is related to the number of electrons, $n$, exchanged in the overall $O_2$ reduction reaction

$$\text{slope} = (0.62nFD_O^2v^{-1/6}(D_O)^{-1})^{-1} \quad [4]$$

where $F$ is Faraday’s constant, $D_O$ is the diffusivity of $O_2$ molecule in the electrolyte, $v$ is the rotation speed, $v$ is the kinematic viscosity, and $C_{O_2}$ is the concentration of $O_2$ in the electrolyte. The fact that the same slope is obtained for both LaCu$_{0.5}$Mn$_{0.5}$O$_3$ and Pt/C confirms the complete 4-electron reduction of $O_2$ to water. Figure 5 also shows the Koutecky–Levich analysis for LaCu$_{0.5}$Mn$_{0.5}$O$_3$, and the essentially identical slope demonstrates the 4-electron reduction to water on LaNiO$_3$, which agrees with previously reported rotating ring-disk electrode (RRDE) measurements on LaNiO$_3$. Unfortunately, because of its low ORR activity ($\sim$0.2 mA cm$^{-2}$ at 0.7 V, see Fig. 3), no Koutecky–Levich analysis could be conducted with the La$_{0.75}$Ca$_{0.25}$FeO$_3$ sample. Even though, in general, the final product of the reduction (i.e., number of electron transferred) must be known to quantify the kinetic ORR current (see Eq. 3), the transport correction term is negligible ($\sim$10%) if the measured current is less than 10% of the minimum limiting ORR current (i.e., assuming a 2-electron reduction), which is the case for the La$_{0.75}$Ca$_{0.25}$FeO$_3$ electrode, so that sufficiently precise kinetic ORR current densities can be obtained even in this case where the final reaction product ($H_2O$ or $H_2O_2$) is unknown.

A cautionary note on the interpretation of the above described Koutecky–Levich analysis or of RRDE measurements is suggested here, as it was shown that the apparent number of electron transferred in the ORR deduced from RRDE measurements can depend on electrode thickness. For example, Fe–N–C–based catalysts were shown to quantitatively reduce $O_2$ to $H_2O_2$ (2-electron process), but because of the facile nonelectrochemical $H_2O_2$ decomposition ($H_2O_2 \rightarrow H_2O + 0.5 O_2$), RRDE measurements on thick electrodes ($>5$ $\mu$m based on the known packing density of high surface area carbons) indicated an apparent mostly 4-electron reduction process on these catalysts. Because the electrode thickness is only $\sim 2$ $\mu$m, we would not expect this artifact and believe that LaCu$_{0.5}$Mn$_{0.5}$O$_3$ and LaNiO$_3$, indeed, reduce $O_2$ in a 4-electron process to water. Nevertheless, to unambiguously identify the ORR product ($H_2O$ vs $H_2O_2$), detailed RRDE measurements of electrodes with varying thickness would be necessary.

To extract the actual ORR kinetics of these oxides and of Pt/C, ohmic drop and mass transport corrections were applied to the ORR measurement using the Levich equation for the convective transport in an RDE configuration (see Experimental section). The resulting kinetic ORR activities were then normalized by the measured specific surface areas of the oxides (Table I) or of Pt/C (see Experimental section) to obtain the specific ORR activity, $i_s$, plotted in Fig. 6. In terms of specific activity, LaNiO$_3$ is the most active of the three studied oxide materials, with a value of $\sim$40 $\mu$A cm$^{-2}$ compared to $\sim$320 $\mu$A cm$^{-2}$ for Pt/C at the typical benchmark condition of 0.9 V vs RHE (Fig. 6). Although there are many previous papers on the use of LaNiO$_3$ as ORR catalyst, specific activities can only be extracted from the study of Bockris and Otagawa with a value of $\sim$0.1 $\mu$A cm$^{-2}$ at a reported roughness factor $\sim$1000 cm$^{-2}$ electrode. The difference between this previously reported low specific activity for LaNiO$_3$ and our measurement can be attributed to undefined $O_2$ mass transport overpotentials in the thick and porous pellet electrodes used, whereby this artifact could be avoided in our thin-film RDE measurements. The Tafel slopes of the three different oxides and of Pt/C (Fig. 6) are all within $\pm 60 \pm 10$ mV dec$^{-1}$. This is consistent with the Tafel slope reported for polycrystalline Pt at the same conditions, reported Tafel slopes for LaNiO$_3$ scatter over a wide range (45 mV dec$^{-1}$, 60 mV dec$^{-1}$, and 120 mV dec$^{-1}$), which again is most likely related to the poorly controlled $O_2$ mass transport in these measurements based on thick porous pellets or gas diffusion electrodes.

Figure 7 shows the ORR mass activity, $i_{mass}$, of the various perovskites and Pt/C. At the typical benchmark voltage of 0.9 V vs RHE, the measured mass activity of Pt/C (0.15 A mgPt$^{-1}$) agrees with the literature (0.12 A mgPt$^{-1}$) [5]. Unfortunately, most studies on the ORR activity of LaNiO$_3$ provide no information on catalyst mass in the electrodes[19,21,39] or lack detailed experimental conditions. Only two studies allow the evaluation of defined LaNiO$_3$ mass activities (pure $O_2$, room temperature, 0.9 V vs RHE corresponding to $\sim$0.02 V vs Hg/HgO), with values of $\sim$2 A g$^{-1}$ (6 M KOH) and $\sim$0.7 A g$^{-1}$ (5 M KOH)[8], which are reasonably consistent with the value of $\sim$1.6 A g$^{-1}$ (0.1 M KOH) obtained from Fig. 7. The
mass activities of LaCu$_{0.5}$Mn$_{0.5}$O$_3$ and La$_{0.75}$Ca$_{0.25}$FeO$_3$ are significantly lower than LaNiO$_3$, and no comparison data are available in the literature.

In the following, we estimate the kinetically limited cathode performance of LaNiO$_3$ and Pt/C if used in a fuel cell based on mass activities shown in Fig. 7. A recent paper compared the cathode performance of La$_{0.6}$Sr$_{0.4}$Mn$_{0.8}$Fe$_{0.2}$O$_3$ with that of a Pt/C at equal loading (1 mg$_{\text{oxide}}$ or 1 mg$_{\text{Pt}}$ per cm$^2_{\text{cathode}}$), showing only $\sim$0.1 V lower performance for the perovskite catalyst. Another study showed essentially identical performance of La$_{0.8}$Sr$_{0.2}$Mn$_{0.8}$Fe$_{0.2}$O$_3$ with that of a Pt/C cathode of, however, undefined Pt loading. In general, it is not straightforward to compare the potential cathode activity of “cheap” oxide catalysts with precious metal catalysts, because the cathode loading of nonprecious metal oxide catalysts is limited only by electrode thickness constraints, while the loading of Pt catalyst is constrained by cost considerations. We assumed that the maximum allowable electrode thickness for an optimized “cheap” oxide catalyst can then be estimated by multiplying the maximum LaNiO$_3$ loading with its mass activity values shown in Fig. 7, with that of a Pt-based cathode with a loading of 0.4 mg$_{\text{Pt}}$ cm$^{-2}_{\text{cathode}}$. At a cathode thickness of $\sim$20 $\mu$m, the assumption that mass transport resistance induced voltage losses could be negligible for optimized electrodes is quite realistic.

From this analysis, the oxide-based cathode performance could indeed be competitive with that of Pt/C, but it is also clear that oxides with higher ORR activity than LaNiO$_3$ are desired with, most importantly, long-term stability over a wider potential range. The establishment of a reliable and fast ORR activity screening method, as presented in this work, can accelerate the development of oxide-based ORR catalysts with enhanced activity and durability. Identifying more active and more durable oxide-based ORR electrocatalysts is the subject of our current work and will be discussed in a future communication, where we will examine the ORR activity of many model perovskites using the thin-film RDE technique with the alkali ion-exchanged Naftan binder presented here. We seek to develop fundamental ORR activity descriptors to more effectively search the large parameter space of partially substituted AA’BB’O$_3$ perovskites, analogous to what was developed for noble metal catalysts.

**Conclusion**

We report a methodology using the thin-film RDE technique to quantify the mass and specific ORR activities of submicrometer-sized oxide catalysts, as poor mass transport in traditional porous electrodes leads to ambiguity in comparing the intrinsic ORR activity of different oxides. Using this method, we show that La$_{0.75}$Cu$_{0.25}$FeO$_3$ has the lowest mass and specific activities, followed by LaCu$_{0.5}$Mn$_{0.5}$O$_3$ and by LaNiO$_3$, which is the most active.

1. For example, the modern modified electrode method for preparing oxide particles in the range of 100 nm or less.
2. Under these idealized conditions, one might compare the kinetically limited performance of a roughly 10 $\mu$m thin Pt-based cathode electrode at a loading of 0.4 mg$_{\text{Pt}}$ cm$^{-2}_{\text{cathode}}$ with that of a roughly 100 $\mu$m thick oxide-based cathode. We emphasized that this projection is based on the above idealized assumptions of negligible transport resistances in an optimally engineered oxide-based electrode, but it nevertheless provides a best-case scenario.
3. The Koutecky–Levich analysis indicates that, for LaNiO$_3$ and LaCu$_{0.5}$Mn$_{0.5}$O$_3$, the reaction proceeds through the 4-electron reduction, thereby increasing the active oxide surface area per mass by a factor of 5. At this particle size, the kinetically limited activity of an oxide-based cathode at a loading of $\sim$7 mg$_{\text{oxide}}$ cm$^{-2}_{\text{cathode}}$ and an estimated thickness of $\sim$20 $\mu$m would equal that of a Pt-based cathode with a loading of 0.4 mg$_{\text{Pt}}$ cm$^{-2}_{\text{cathode}}$. At a cathode thickness of $\sim$20 $\mu$m, the assumption that mass transport resistance induced voltage losses could be negligible for optimized electrodes is quite realistic.
nanoparticles supported on carbon, where catalyst loading is constrained by cost instead. Our work establishes a fast, reliable technique to screen submicrometer-sized catalysts, which can aid in the development of highly active and low cost ORR catalysts.

Acknowledgment
The authors acknowledge significant contributions to this work by Dr. Haruyuki Nakanishi and Hidekazu Arikawa from the Toyota Motor Co.

Massachusetts Institute of Technology assisted in meeting the publication costs of this article.

References