Highly Active, Non-precious Metal Perovskite Electrocatalysts for Bifunctional Metal Air Battery Electrodes

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Experimental

All chemicals were used as received. Anhydrous ethanol and 5 wt % nafion solution in lower alcohols were purchased from Sigma-Aldrich. Nickel(II) nitrate hexahydrate (99%), lanthanum(III) nitrate hexahydrate (99.999%), tetrapropylammonium bromide (TPAB, 98%), tetramethylammonium hydroxide pentahydrate (TMAOH, 99%), 2-propanol and potassium hydroxide were obtained from Fisher Scientific, and ethanol (Absolute 200 proof) from Aaper alcohol. Millipore high purity water (18 M Ω) was used. Oxygen (research grade, 99.999% purity) and argon (research grade, 99.999% purity) were obtained from Praxair. Nitrogen doped carbon (NC) was prepared as reported elsewhere.¹

Catalyst Synthesis

Particle Synthesis. Amorphous particles composed of nickel and lanthanum hydroxides were prepared by slowly dripping (~ 2 mL/min) an aqueous metal nitrate solution into concentrated base containing dissolved TPAB, as reported previously.²⁻⁵ Briefly, equimolar amounts of La(NO₃)₃ and Ni(NO₃)₂ were dissolved under stirring in 50 mL of DI water, such that the total metal concentration was 9.9 mM. Separately, an equimolar amount of TPAB relative to metal nitrates was dissolved into 200 mL of 1 wt% TMAOH (pH 14) under vigorous stirring. The metal nitrate solution was slowly dripped (~ 2 mL/min) into the stirred base. The solution was left stirring for ~ 1 hour, collected and centrifuged at 8000 RPM for 4 min which resulted in a gelatinous green pellet. The gel was washed with DI water and centrifuged to obtain the final gel of amorphous particles.

Particle Harvesting and Crystallization. For oven dried samples, the washed hydroxide gel was spread over a glass dish and dried at 120°C under air for a minimum of 1 hour. The dried powder was collected and calcined at 700°C for 4 hours under flowing air (~ 120 mL/min). For samples harvested by thin film freezing (TFF), the washed hydroxide gel was dispersed in 100 mL of DI water and probe sonicated. The experimental apparatus for TFF has been described elsewhere.⁶ Briefly, a hollow metal drum was filled with dry ice and 2-propanol ($\sim 2:1$ v/v) and rotated at 5 RPM. A metal plate with a tapered edge was fastened so that the plate edge grazed the drum surface. A recrystallization dish was placed directly

under the plate and filled with liquid N₂. The particle solution was slowly pipetted (3 mL/min) onto the rotating drum, whereupon it froze and was subsequently scraped by the plate into the dish. Lyophilization was performed at -10°C and a fixed pressure of ~50 mTorr for 20 hours to remove all traces of water. The lyophilized powder was calcined at 700°C for 4 hours under flowing dehumidified air. Following calcination, all particles were washed with EtOH and filtered to obtain the final LaNiO₃ catalyst. All catalysts, except for those explicitly noted as unsupported, were loaded to 30wt% by mass of perovskite on nitrogen doped carbon (NC) by mixing with ball milling for 3 minutes using a Wig-L-Bug. The synthesis of the carbon composite is described elsewhere.¹

Dynamic light scattering (DLS). The hydrodynamic diameter (D_{HS}) of as-synthesized hydrolysis particles was measured with a Brookhaven ZetaPALS instrument with the ZetaPlus option. Scattered light was collected with a 90° avalanche photodiode detector and all data were fit with the CONTIN routine. The diameter of as-synthesized metal hydroxide particles were measured at a concentration of ~1 mg/mL in DI water. All measurements were made over a period of 3 min and repeated in triplicate.

X-ray Diffraction (XRD). Wide-angle X-ray diffraction was performed on a compact powder of carbon supported catalyst on a quartz slide with a Bruker Nokius AXS D8 Advance instrument using Cu K α radiation (1.54 Å wavelength). Samples were scanned from 20 to 90 degrees in 0.02 degree increments with a dwell time of 4 seconds. The average crystallite size was estimated from the Scherrer equation. Background correction, fitting, and deconvolution were done using JADE software (Molecular Diffraction Inc.).

Electron Microscopy. Scanning (transmission) electron microscopy (SEM/STEM) was performed with a Hitachi S-5500 using a 30 kV accelerating voltage and a probe current of 20 μ A. The carbon supported catalysts were deposited from a dilute ethanol suspension onto a 200 mesh copper grid coated with lacey carbon or Formvar (Electron Microscopy Sciences).

Surface Area Analysis. Nitrogen sorption analysis was performed on a Quantachrome Instruments NOVA 2000 high-speed surface area BET analyzer at a temperature of 77 K. Prior to measurements, the

samples were degassed in vacuum for a minimum of 12 hours at room temperature. The specific surface area was calculated using the BET method from the nitrogen adsorption data in the relative pressure range (P/P_0) of 0.05 to 0.30.

X-ray Photoelectron Spectroscopy (XPS). XPS data was acquired using a Kratos AXIS Ultra DLD spectrometer equipped with a monochromatic Al X-ray source (Al α , 1.4866 keV). High resolution elemental analysis was performed on the N 1s, O 1s and La/Ni 3d core regions with a 20 eV pass energy, 0.1 eV steps, and a 4 second dwell time. Charge compensation was not used as each sample was conductive. All absolute energies were calibrated relative to gold, silver and graphite. The peak positions and areas are calculated using a standard sum Gaussian-Lorentzian fit with a linear (N, O) or Shirley (La/Ni) background correction.

Electrochemical Characterization

Catalyst inks were prepared by adding 1 mL of a NaOH neutralized 0.05 wt% Nafion solution⁷ to 1 mg of catalyst powder and bath sonicated for 30 minutes. A volume of ink (10 μ L) was drop cast onto a clean 5mm (0.196 cm², Pine Instruments) glassy carbon electrode and dried under a glass jar at ambient conditions. The glassy carbon electrodes were cleaned prior to drop casting by sonication in a 1:1 DI water:ethanol solution. The electrode was then polished using 0.05 μ m alumina powder, sonicated in a fresh DI water:ethanol solution, and dried in ambient air. All electrochemical tests were performed on electrodes prepared by this method, yielding a catalyst loading of 51 μ g/cm² (15.3 μ g_{oxide}/cm² for carbon supported LaNiO₃).

Electrochemical testing was performed on either a CH Instruments CHI832a or a Metrohm Autolab PGSTAT302N potentiostat, both equipped with high speed rotators from Pine Instruments. All testing was done at room temperature in 0.1 M KOH (measured pH $\approx$ 12.6). The current interrupt and positive feedback methods were used to determine electrolyte resistance (50 Ω) and all data was iR compensated after testing. Each test was performed in a standard 3 electrode cell using a Hg/HgO (1 M KOH) reference electrode, a Pt wire counter electrode, and a film of catalyst ink on glassy carbon as the working

electrode. All potentials are reported versus the regular hydrogen electrode (RHE), which was shifted +0.843 V vs. Hg/HgO (Hg/HgO (1 M KOH) + 0.1 V = NHE; NHE + 0.059 * pH = RHE).

Quantification of Oxygen Reduction Activities. The electrolyte was saturated with oxygen by bubbling for a minimum of 10 minutes. ORR activity measurements were taken by rotating the electrode at 1600 rpm and performing a linear sweep from 1.043 V to 0.243 V RHE at 5 mV/s. Kinetic currents were used to evaluate mass activities for the ORR and were taken at 0.693 V RHE from the polarization curves. The kinetic ORR current was calculated according to the Koutecky-Levich equation: $\frac{1}{i} = \frac{1}{i_d} + \frac{1}{i_k}$. Data reported herein is the average mass activity taken from cathodic scans of multiple electrodes.

Quantification of Oxygen Evolution Activities. Immediately following ORR measurements, the electrolyte was saturated with argon by bubbling for a minimum of 10 minutes. OER activity measurements were taken upon rotating the electrode at 900 rpm and performing a linear sweep from -0.057 to 1.943 V at 50 mV/s.⁸ Kinetic OER currents could not be calculated due to the lack of a well-defined diffusion limited regime, as the result of interference from the oxygen bubbles. The current at 1.63 V (representing a 400 mV overpotential) was determined from the polarization curves and used to characterize the OER mass activity. To enable comparison with OER data in the literature, scans were also performed from 0.9 V to 1.943 V at 10 mV/s with a rotation rate of 1600 rpm in O₂ saturated 0.1 M KOH. O₂ saturated OER testing was performed on a new electrode which had not undergone any previous testing. The current at 1.56 V was taken from the polarization curves to compare the OER activities to values reported in literature. Note that at potentials above 1.6 V in oxygen saturated media, visible oxygen bubble formation on the electrode surface interfered with the ability to accurately measure the activity. Data reported herein is the average mass activity taken from anodic scans of multiple electrodes.

Bifunctionality Comparison

It should be noted that the OER data reported by Gorlin, et. al.⁹ for Ir/C and Pt/C was collected at 5 mV/s, whereas the OER data reported herein was taken at 10 mV/s. Capacitive current contributions in

the LaNiO₃/NC system were found to be negligible, which enables a fair comparison. Figure S4 shows the capacity corrected OER polarization curve, in which $j = 10 \text{ mA/cm}^2$ occurs at 1.660 V RHE.

Figure S1. SEM micrographs of particles calcined at 700°C in air. These particles were crystallized from A/B) amorphous particles processed with thin film freezing followed by lyophilization (‘freeze drying’), producing a thin film of sintered particles and C/D) amorphous particles dried in an oven at 120°C, resulting in larger particles with lower surface area.

Table S1. Summary of particle size, size, crystallite size and BET measured surface area.

catalyst	DLS size [nm]*	SEM [nm]**	XRD [nm]***	BET [m ² /g]
LaNiO ₃	25 ± 5	20-400	15	6
nsLaNiO ₃	25 ± 5	~50	14	11

* As-synthesized amorphous precursor particle sizes

** After calcination, size of crystallites

*** Crystallite size after calcination, Scherrer analysis on {024} reflection

Figure S2. BET adsorption curves for unsupported nsLaNiO₃ and LaNiO₃, used to calculate respective surface areas of 11 m²/g and 6 m²/g.

Figure S3. BET adsorption curve and pore size distribution (PSD) for NC indicating a surface area of 1080 m²/g and pore volume 1.07 cm³/g. The PSD shows the carbon is primarily composed of mesopores in the range of ~10 nm.

Figure S4. OER polarization curves for both iR corrected and uncorrected nsLaNiO₃/NC in O₂ saturated 0.1 M KOH at 1600 rpm and 10 mV/s. The anodic and cathodic scans (same electrode) are shown prior to iR correction, and the average of both scans has been taken and iR corrected to illustrate the lack of capacitive current contributions to the total observed current. The iR corrected average scan has an OER mass activity of 89 mA/mg_{oxide} at 1.56 V RHE, identical to corrected anodic and cathodic scans. Additionally, the potential at which $J = 10 \text{ mA/cm}^2$ is shifted by less than 0.5 mV when the iR corrected average scan is compared to either anodic or cathodic. Additionally, the lack of hysteresis indicates that the catalyst doesn't undergo any irreversible (electro)chemical changes during anodic cycling.

Figure S5. Tafel plot of the iR corrected average OER polarization curve (Figure S4) for nsLaNiO₃/NC in O₂ saturated 0.1 M KOH at 1600 rpm and 10 mV/s. Note that the linear fit was performed over the potential region of ~1.525 to 1.625 V, yielding a slope of 42 mV dec⁻¹ with a R² of 0.9994.

Figure S6. The proposed alkaline oxygen evolution cycle on LaNiO_3 , including the direct participation of lattice (hydr)oxide ions in the formation of surface hydroperoxide (step 3), resulting in a lattice vacancy that is subsequently replenished from the bulk electrolyte (step L). Surface lattice (hydr)oxides are distinguished from solution hydroxide ions by (H)O^- , signifying their possible protonated state.

Figure S7. High resolution XPS spectra of the N 1s core region for neat nsLaNiO₃, nsLaNiO₃/NC and pure NC, which includes proposed peak deconvolution for pure NC and nsLaNiO₃/NC. Note the high percentage of pyridinic functionality in both spectra.

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