Role of lattice oxygen content and Ni geometry in the oxygen evolution activity of the Ba-Ni-O system

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HIGHLIGHTS

- BaNiO$_x$ display high intrinsic OER activity.
- Ni's coordination and oxidation state determine the OER activity in BaNiO$_x$.
- Square planar Ni environments are more active than octahedral Ni for the OER.

GRAPHICAL ABSTRACT
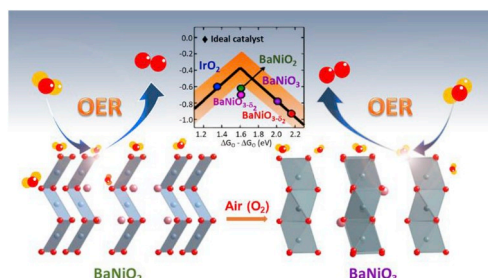
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ABSTRACT

The activity of oxides towards the oxygen evolution reaction (OER) is usually tuned by changing the transition metal components and/or the surface facets. An important yet less studied feature is the repercussion of the lattice oxygen content of the oxide in the active site's coordination and catalytic performance. This is illustrated here for the Ba-Ni-O system. We synthesized two oxides with Ni in different coordination and oxidation states, namely BaNiO$_2$ with Ni^{2+} in square-planar positions, and BaNiO$_{2.78(2)}$ with Ni^{3+} and Ni^{4+} in octahedral positions. We show that the square-planar configuration of Ni endows BaNiO$_2$ with high intrinsic OER activity, comparable to the best catalysts in the literature. DFT indicates that progressively lowering the lattice oxygen content from BaNiO$_3$ to BaNiO$_2$ increases the Ni sites' affinity for the reaction intermediates, thereby lowering the OER overpotential. Thus, oxygen content is an important parameter in oxide catalysts, as it modulates the coordination, orbital splitting, oxidation number, and catalytic activity of the active sites.

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1. Introduction

Water electrolysis using renewable energy is arguably the cleanest way of producing hydrogen or, said another way, of accumulating renewable energy in chemical bonds. However, the efficiency of this process is still limited, especially due to the sluggish kinetics of the oxygen evolution reaction (OER), namely the formation of oxygen from water in the anode [1]. The OER is also essential for rechargeable metal-air batteries and CO_2 electrolyzers. Currently, Ru- and Ir-based oxides are the state-of-the-art catalysts for the OER [2,3]. However, the expensiveness and scarcity of Ir and Ru call for the use of more abundant and less costly materials. Ni-based catalysts such as Ni oxides, hydroxides and oxy-hydroxides exhibit high OER activity in alkaline media, and the incorporation of other metals such as Fe, Co, Mn or Cr can enhance their activity [4–7].

Perovskites are also promising OER catalysts, especially in alkaline media [8–13]: $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (1.42 mA cm_{disk}^{-2}), $La_{0.5}Ca_{0.5}CoO_3$ (1 mA cm_{disk}^{-2}), and $SrCo_{0.8}Fe_{0.2}O_3$ (3.5 mA cm_{disk}^{-2}) at 1.6 V [9,14–17] are to date the most active ones without noble metals in the structure. However, they are prone to cation dissolution and segregation, which compromises their durability [16]. Ni mixed oxides display a good activity and stability balance [4]. For example, $LaNiO_3$ reaches 0.05 mA cm_{oxide}^{-2} at 1.56 V [8] and $BaNiO_3$ 2.5 mA cm_{oxide}^{-2} at 1.6 V [18]. The latter has a hexagonal structure related to perovskite [19], where the metal active sites share faces in one direction with the following octahedra, instead of sharing corners as in regular perovskites.

Other compounds with this hexagonal structure have also shown high OER activity, such as $Sr_6Co_5O_{15}$ with an activity of 10 mA cm_{oxide}^{-2} at 1.6 V [20]. Importantly, oxygen-deficient perovskites (brownmillerite, $A_2B_2O_5$) can display higher OER activities than stoichiometric perovskites (ABO_3) [17]. This is the case of $Ca_2Mn_2O_5$ with active sites at oxygen square pyramid units and OER activity of 1.64 A g^{-1} at 1.5 V, higher than that of the stoichiometric $CaMnO_3$ perovskite (0.47 Ag^{-1} at 1.5 V) [21]. Other perovskite geometries also have high activity: $Ca-Cu_3Fe_4O_{12}$ displays 0.5 $mAcm_{oxide}^{-2}$ at 1.54 V and it has been suggested that its high activity is related to the CuO_4 square-planar and FeO_6 octahedral units [22].

In this work, we illustrate that although the chemical identity of metal centers is believed to be the main parameter controlling the OER activity of oxides, the spatial distribution and number of oxygen ligands play also an important role. Here, we assess the optimal configuration for the OER activity of the Ba-Ni-O system and conclude that square-planar units of Ni^{2+} offer nearly optimal conditions for the OER. We note that our main goal here is not just the design of a new electrocatalyst per se, but also the elucidation of the effect of an important parameter such as oxygen content on the OER activity of an oxide system. This is motivated by the fact that systematic studies in the phase space of metal oxides are uncommon and habitually restricted to inspecting different facets [2]. At the end of the discussion we will also consider the stability of the studied catalysts.

2. Methods

2.1. Synthesis Ba-Ni-O

Barium peroxide (BaO_2) and nickel oxide (NiO) are used as starting materials. The oxides are finely mixed and grounded, heated at 450 °C during 12 h in air. In order to form $BaNiO_2$ while preventing further oxidation to $Ba_3Ni_3O_8$ or similar phases, the solid obtained was thermally treated at 1000 °C in N_2 flow for 12 h. We show the topotactic relationship between $BaNiO_2$ and $BaNiO_3$ by preparing the latter by mild thermal treatment of the former at 600 °C in air during 12 h.

2.2. Physicochemical characterization

The phase identification and purity was determined by x-ray powder diffraction (XRD) in the Bragg-Brentano reflection geometry with CuK_α radiation (λ = 1.5418 Å). A detailed crystallographic study was performed by using Powder Neutron Diffraction (PND) in the Siloé reactor, CEN-Grenoble, France, collected at room temperature and λ = 1.4326 Å. The refinement of the crystal structures was performed using the Rietveld method and the Fullprof crystallographic program [23,24]. Pseudo-Voigt function was used to generate the shape of the diffraction peaks. In the final refinement the scale factor, background coefficients, zero-point error, pseudo-Voigt corrected for asymmetry parameters, positional coordinates, isotropic thermal factors an occupancy factors for oxygen atoms are refined.

N_2 adsorption-desorption isotherms were recorded at liquid N_2 temperature with a Micromeritics ASAP 2000 apparatus to evaluate textural properties. The samples were degassed at 140 °C under vacuum for 24 h. Specific areas were calculated by applying the BET method within the relative pressure range P/P_0 = 0.05–0.30.

High-resolution electron microscopy (HRTEM) and x-ray energy dispersive spectra (EDS) were recorded in a JEOL 2100 field emission gun transmission electron microscope operating at 200 kV and equipped with an EDS spectrometer Oxford INCA Energy 2000 system. The specimens were prepared by depositing aliquots of the sample onto a Cu grid supporting a lacey carbon film.

X-ray photoelectron spectra (XPS) were acquired with a VG ESCALAB 200 R at a pass energy of 50 eV using a Mg Kα x-ray source. The kinetic energies of the photoelectrons were measured using a hemispherical electron analyser working in the constant-pass energy mode. The background pressure in the analysis chamber was kept below 3×10^{-8} mbar during data acquisition. At least 200 scans were collected in increments of 0.1 eV with dwell times of 50 ms in order to increase the signal-to-noise ratio. Binding energies ($\pm$ 0.2 eV) were determined by setting the C 1s peak at 284.8 eV.

X-ray Absorption Spectroscopy (XAS) measurements were performed at room temperature at Diamond Light Source (UK) on the B18 beamline [25]. Data were collected at Fe-K edge (E = 7112 eV) in the transmission mode using a double crystal Si111 monochromator and Pt-coated branch. A pair of harmonic rejection mirrors was used to act as low-pass filter and cut off the higher energy portion of photons still present in the beam. XAS data treatment and linear combination fits were achieved with the ATHENA software [26]. XANES simulations were performed by means of the FEFF8.4 code [27].

2.3. Electrochemical characterization

An Autolab PGstat 302 N potentiostat/galvanostat was used to test the electrochemical performance of the oxides. The measurements were performed using a standard three-compartment glass cell and a rotating disk electrode (RDE) (Pine Research Instruments). A gold wire and a homemade Reversible Hydrogen Electrode (RHE) were used as counter and reference electrodes, respectively. The oxides were deposited on top of the working electrode by means of an ink. The inks were prepared by mixing 5 mg of oxide and 1 mg of carbon black (Vulcan-XC-72R). This carbon is used to improve the electrical conductivity. The solids were ultrasonically dispersed in tetrahydrofuran (THF) and Nafion using an Ultrasonic Processor UP50H (Hielscher). The composition of the ink was 5 mg_{oxide}, 1 mg_{vulcan}, 0.03 mL_{Nafion} and 0.97 mL_{THF}. 20 μL of ink were dropped onto a glassy carbon electrode of 0.196 cm^2 of area, with a catalyst loading of 0.5 mg_{oxide} cm^{-2}.

To measure the oxygen evolution reaction we recorded several voltammograms between 1.1 and 1.7 V at 10 mVs^{-1} until a reproducible voltammogram was obtained. The measurements were performed in an O_2 saturated 0.1 M KOH electrolyte to assure the O_2/H_2O equilibrium at 1.23 V, at a rotation rate of 1600 rpm. The OER kinetic curves were capacitance-corrected by using the average of the anodic and cathodic curves and iR-corrected by using the formula E-$iR_{corrected}$ = $E_{applied}$ − iR. In this formula i is the current and R is the ohmic electrolyte resistance (R ∼29 Ω) as obtained from