



Tuning Composition and Activity of Cobalt Titanium Oxide Catalysts for the Oxygen Evolution Reaction



Linsey C. Seitz^a, Dennis Nordlund^b, Alessandro Gallo^c, Thomas F. Jaramillo^{a,c,*}

^a Department of Chemical Engineering, Stanford University, Shriram Center, 443 Via Ortega, Stanford, California 94305, USA

^b SSRL, SLAC National Accelerator Laboratory, 2575 Sand Hill Rd, Menlo Park, California 94025, USA

^c SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Rd, Menlo Park, California 94025, USA

ARTICLE INFO

Article history:

Received 18 November 2015

Received in revised form 7 January 2016

Accepted 12 January 2016

Available online 29 January 2016

Keywords:

Electrocatalysis

Water oxidation

X-ray absorption spectroscopy

ABSTRACT

Understanding catalyst function to improve activity for the oxygen evolution reaction (OER) is key to increasing the overall efficiency of electrochemical water splitting, a promising method for sustainable and clean production of hydrogen. Using a straightforward and scalable sol–gel synthesis, we explore the effects of metal composition in $\text{Co}_x\text{Ti}_{1-x}\text{O}_y$ on electrochemical activity, atomic structure, and electronic state. Physical and electronic characterization reveal that increased amounts of Ti stabilize the 2+ oxidation state of the Co precursor and lead to formation of less active CoO-like catalysts. Conversely, films with Co:Ti ratios of 1:1 or greater result in catalysts with high activity, correlating with greater Co 3+ character, as measured by *ex situ* XAS for samples as-prepared and after exposure to OER conditions. Additionally, decreasing the Ti content systematically shifts the Co redox potential from approximately 1.5 V vs. RHE with a 1:3 Co:Ti ratio to 1.0 V vs. RHE with no Ti, further evidence that Ti stabilizes Co in a lower oxidation state. Controlling the oxidation state of metals in metal-oxide OER catalysts can have a profound effect on catalytic activity.

© 2016 Published by Elsevier Ltd.

1. Introduction

Electrochemical water splitting is a promising method for producing hydrogen, a chemical commodity currently consumed at a rate of 50 billion kilograms per year, primarily for fertilizer [1]. If this process is coupled to a renewable energy source, such as wind or solar, water splitting could provide a sustainable, clean method for production of hydrogen to replace current industrial methods and could also expand hydrogen's use as a renewable fuel. Water splitting consists of two half-reactions, the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). The OER is the more complex of the two reactions and requires large overpotentials to proceed at relevant current densities, which severely limits the overall efficiency of water splitting [2,3]. Fundamental studies to better understand material function and development of improved catalysts are needed to make further progress for this promising technology.

Among the best catalysts for this reaction are precious metal oxides, RuO_2 and IrO_2 , but extensive research has been conducted

on development of nonprecious metal oxides such as MnO_x , CoO_x , CoFeO_x , and NiFeO_x to mitigate high cost and scarcity of precious metals [4–19]. Extensive work on perovskites and double perovskites, many of which include Co, has resulted in development of very high activity catalysts, such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ [20–23]. Additionally, theoretical studies have investigated active phases of CoO_x catalysts as well as predicted methods for further optimization of other OER catalysts by tuning their electronic levels through alloying or introduction of dopants [24–26].

In our previous work, we identified CoTiO_x as a novel, nonprecious metal catalyst for the OER which can be synthesized using a facile sol-gel technique and deposited on a variety of substrates [27]. The most active catalysts were produced with low calcination temperatures and a metal composition of 50% Co and 50% Ti (based on the relative amounts of respective precursors in the sol-gel). Expanding upon this work, we investigate the effects of varying the metal composition on the local geometric structure, activity, and electronic structure of this material system.

This study involves the use of both hard X-rays and soft X-rays in spectroscopic studies of local structure and chemical state of these catalysts. Extended X-ray absorption fine structure (EXAFS) is employed to determine effects of material composition on the local structure of materials, even in the absence of long range order,

* Corresponding author at: Department of Chemical Engineering, Stanford University, Shriram Center, 443 Via Ortega, Stanford, California 94305, USA.
E-mail address: jaramillo@stanford.edu (T.F. Jaramillo).

which is important as the highest activity catalysts exhibit low crystallinity since high-temperature calcination steps were avoided [27,28]. Hard X-rays are used to probe number and location of atoms surrounding a central X-ray absorbing atom via interference patterns. Interactions between the backscattered electrons of neighboring atoms and waves of the emitted photoelectrons from the central atom result in oscillations above the absorption edge. The Fourier transform of these oscillations reveals a pattern of distinct peaks which can be used to identify structural motifs consistent with known crystalline materials. Structural data from EXAFS are also correlated with results from soft X-ray absorption spectroscopy (XAS) which probe the material surface electronic structure, which is particularly relevant for these electrochemical catalysts. *Ex situ* soft XAS is a powerful tool which can be used to determine oxidation state and element-specific electronic structure information. The use of soft X-rays allows one to probe the valence structure of first row transition metals including fine spectral features caused by multiplet effects. The use of both hard and soft X-rays in this study provides a distinctive insight into the local structural details and the surface oxidation state of the catalyst which could not be understood with only bulk sensitive or non-synchrotron techniques.

2. Experimental Methods

2.1. Sample Preparation

A sol-gel was prepared using a published procedure; briefly, cobalt acetate (Sigma-Aldrich, 99.999% trace metals basis) and titanium (IV) isopropoxide (Sigma-Aldrich, 99.999% trace metals basis) were dissolved separately in 2-methoxyethanol (Acros Organics, extra pure, >99%) [28]. Varying ratios of the two precursor solutions were mixed and diluted 4 fold to produce films ranging in metal composition from 100% Co and 0% Ti to 0% Co and 100% Ti. Fluorine-doped tin oxide (FTO) substrates on aluminoborosilicate or fused silica (Solaronix, sheet resistance of $10 \Omega/\text{sq}$) were ultrasonically cleaned using acetone and isopropanol and then dipcoated in the sol-gel solutions. All samples were heated in air in a fused silica tube furnace (Mellen Company) for two hours at 150°C .

2.2. Assessment of Material Surface Composition

X-ray photoemission spectroscopy (XPS) was used to determine the relative amounts of Co and Ti at the film surface for each sample. XPS was performed using a Phi VersaProbe spectrometer with an Al $K\alpha$ source. Film surface compositions were determined using MultiPak (Physical Electronics, Inc.) fitting software to determine an appropriate baseline and multiply relative areas by sensitivity factors for Co and Ti.

2.3. Identification of Local Structure

A separate set of samples was prepared on bare fused silica substrates (Chemglass Life Sciences) to avoid signal from FTO. *Ex situ* extended X-ray absorption fine structure (EXAFS) was used to measure structural information for these materials since all films were found to lack long range order in X-ray diffractograms. Cobalt K edge (7709 eV) measurements were performed at the 20-pole, 2.0-Tesla Wiggler beamline 4-1 at the Stanford Synchrotron Radiation Lightsource (SSRL) with a Lytle fluorescence detector. Four separate scans for each sample were analyzed using the Demeter software package and a linear pre-edge function was subtracted and the data were normalized by edge height using Athena software [29]. A smooth, third order polynomial approximating the absorption background of an isolated atom was

subtracted to yield $\chi(k)$. The data were then k^3 -weighted and Fourier transformed to reveal reduced distances to cobalt nearest neighbors. The coordination number (N), the distance of the scattering atoms (R), and the mean-squared displacement (σ^2) of the neighboring scatterers were obtained by non-linear fitting with least-squares refinement of the first shell (1.0–2.2 Å) in R-space using the EXAFS equation as implemented in the Artemis software [30]. The Co K amplitude reduction factor (S_0^2) was set to 0.9 and the shift in threshold energy (ΔE_0) was allowed to vary.

2.4. Electrochemical Testing

The catalytic activity was assessed using cyclic voltammetry (CV, BioLogic, VSP) in a 3 electrode electrochemical compression cell made of polytetrafluoroethylene with an exposed working electrode area of 0.5 cm^2 . Fresh samples were swept from 0.95–1.90 V vs. RHE at a scan rate of 25 mV/s in 0.1 M KOH (Sigma-Aldrich, 99.99% trace metals basis). A coiled platinum wire counter electrode and Ag/AgCl 4 M KCl (Fisher Scientific, Accumet) reference electrode were used. All data were post corrected for 100% of the solution series resistance measured by impedance spectroscopy and shifted to a reversible hydrogen electrode (RHE) scale.

2.5. Identification of Surface Oxidation State

Ex situ soft X-ray absorption spectroscopy (XAS) on the cobalt L edge was used to probe the surface oxidation states of the catalyst as prepared and after exposure to OER conditions. To investigate samples under approximated OER conditions, identical samples were electrochemically swept to two different potentials (1.65 or 1.90 V vs. RHE), held for 10 minutes, and removed from the electrolyte under potential control such that the surface remained in its oxidized state. XAS measurements were performed on the 31-pole wiggler beamline 10-1 at SSRL using a ring current of 500 mA and a 1000 lines $\cdot\text{mm}^{-1}$ spherical grating monochromator with 40 μm entrance and exit slits, providing $\sim 10^{11}$ photons $\cdot\text{s}^{-1}$ at 0.3 eV resolution in a 1 mm^2 beam spot. All data were acquired in a single load at room temperature and under ultrahigh vacuum (10^{-9} Torr). Total electron yield (TEY) was measured via the sample drain current and all spectra were normalized by the incoming flux, measured from a thin grid with freshly evaporated gold positioned upstream of the sample chamber. A cobalt oxide reference sample, intercepting a few percent of the beam upstream and recorded simultaneously, was used to calibrate the energy of all scans with a relative energy precision of ± 25 meV. Reference powders were purchased (lithium cobalt(III) oxide, Sigma-Aldrich, 99.8% trace metals basis, cobalt(II,III) oxide, Sigma-Aldrich,

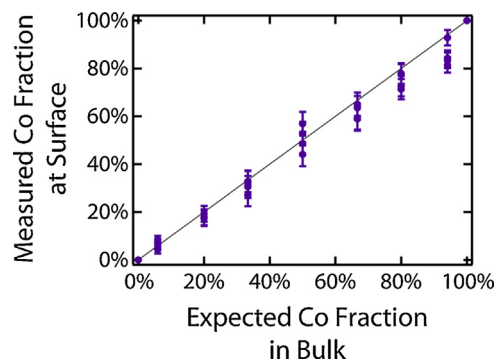


Fig. 1. Surface composition of $\text{Co}_x\text{Ti}_{1-x}\text{O}_y$ films as determined by XPS compared to the expected bulk metal composition based on values of x ranging from 0 to 1. The gray line indicates where the measured Co surface composition equals the expected Co bulk composition.

Download English Version:

<https://daneshyari.com/en/article/183223>

Download Persian Version:

<https://daneshyari.com/article/183223>

[Daneshyari.com](https://daneshyari.com)