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Transition metal doping effects in Co-phosphate catalysts for water splitting studied with XAS

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ABSTRACT

Metal oxides as oxygen evolution reaction (OER) catalysts for water splitting are ubiquitous in research and application. Pure and doped (or hybrid) Co oxide systems are of particular interest due to their good efficiency. However, the electronic effects of different dopants are still unclear in many of these systems. We present a study of doped Co-phosphate (P_i) films deposited electrochemically from aqueous solutions of neutral pH using an X-ray absorption spectroscopy (XAS), a technique that can reveal important information about catalytically active states. These hybrid films, obtained from solutions containing both Co ions and another transition metal (TM) ion (TM = Mn, Fe, Ni), were analyzed with XAS at the TM L-edges and the O K-edge. We find that a large concentration of Co^{3+}-ions in the films and a low-lying edge of the O 2p conduction band (CB) are good indicators for the OER efficiency of the films. Our results show that native Co-P_i is close to optimal for the OER activity at low deposition potential. However, Mn- and Ni-doped systems have promising properties when deposited at higher potentials because these ions tend to stabilize the Co^{3+}-state in the films as well as the position of the O 2p-edge CB (a few tenths of 1 eV), in contrast to native Co-P_i films.

1. Introduction

Society's ongoing transition from its fossil fuel based economy to renewable energy sources arguably presents one of its greatest technological challenges in the modern era. The intermittent nature of e.g. solar, wind, and wave power has led to an increase in the demand for efficient and large scale energy storage. Electrochemical hydrogen fuel production by water splitting – preferably of natural waters – carries promise for such an environmental friendly energy storage. However, electrochemical water splitting requires the oxidation of water in the oxygen evolution reaction (OER) at the anode side. Thus the right choice of catalyst is crucial to ensure energy efficient conversion in this essential step. Future implementation in large-scale energy conversion applications relies on good efficiency with respect to both cost and energy. To this end, cheap and earth-abundant materials like Co and Ni, as well as combinations with different adjacent transition metal (TM) dopants, have been proven to be promising candidates due to their favorable catalytic properties [1]. However, more knowledge about these materials is essential before they can become a true alternative for using expensive noble metals.

In the year 2008, Nocera and co-workers introduced a Co-based oxygen-evolving (OE) catalyst, Co-P_i, that forms upon anodic polarization in neutral, phosphate buffered aqueous solutions, operating at pH 7 with a low overpotential of 0.41 V at 1 mA/cm^2 [2–5]. Recently, Cobo et al. showed that also a hydrogen-evolving electrocatalytic material, nanoparticulate H_2-CoCat, could be obtained from similar electrolyte solutions with low overpotentials that is convertable on anodic equilibration into Co-P_i [6]. Friebel et al. used RIXS and high-resolution XAS to study Co oxide electrocatalysts to investigate the change of oxidation state and to monitor the relation between structure and activity of the catalysts [7]. On the other hand, hybrid systems with several TM's may lead to even more favorable catalyst properties. For instance, it has very recently been shown that introducing Fe to a NiOOH-based OE catalyst alters the oxidation state of Ni thereby improving the catalyst properties [8]. Finally, another recent study of a high-performance hybrid oxide catalyst of manganese and cobalt for low-pressure methanol synthesis [9] further highlights the versatility of combining TM's for enhancing catalyst performance.

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Table 1
Overview of preparation parameters for both high and low deposition potential (DP) sample sets: electrodeposition potentials E_{DP} and the aqueous solutions' ion concentrations c of PO_4^{3-}, Co^{2+}, and transition metal ions ($TM = Mn^{2+}$, Fe^{3+}, Ni^{2+}). The overpotentials η for the low DP films are not iR-drop adjusted and taken at 1 mA/cm^2 *except for NiCo-P$_i$, which is taken at 0.5 mA/cm^2.

Sample	E_{DP} [V vs. NHE]	$c(PO_4^{3-})$ [mM]	$c(Co^{2+})$ [mM]	c(TM) [mM]	η [V]
High DP					
Co-P$_i$	1.85	60	0.20	N/A	N/A
MnCo-P$_i$	1.85	60	0.20	0.22	N/A
FeCo-P$_i$	2.70	60	0.20	0.14	N/A
NiCo-P$_i$	1.85	60	0.20	0.20	N/A
Low DP					
Co-P$_i$	1.30	100	0.5	N/A	0.52
MnCo-P$_i$	1.30	100	0.25	0.25	0.57
FeCo-P$_i$	1.30	100	0.25	0.25	0.56
NiCo-P$_i$	1.30	100	0.25	0.25	0.56*

More fundamental understanding of how a particular TM-dopant affects the electronic properties of hybrid catalyst films is required to achieve higher OER efficiency. Here, we present an XAS study in which we investigate how dopants and different preparation conditions affect the OER in Co-phosphate based hybrid (TM-Co-P$_i$) catalysts. From this study we can identify key properties that efficient hybrid films should possess, namely an abundance of Co^{3+}-ions and a low-lying conduction band edge. For low deposition potentials, native Co-Pi films are superior while Mn- and Ni-doping provide more stability at higher deposition potentials.

2. Experimental

2.1. Electrochemical sample preparation

Catalytic water splitting Co-P$_i$-films have been prepared ex situ with an admixture of another TM (Mn, Fe, Ni) via electrodeposition on conducting, fluorine-doped tin oxide covered (FTO) glass substrates. Two sets of films have been synthesized under different conditions and with varying deposition parameters, which are shown in Table 1. Next to slightly different ion concentrations of the aqueous solutions the two sets differ most notably in their electrodeposition potentials, and hence are referred to as high and low deposition potential (DP) films throughout this paper. The electrodeposition was performed by immersing the FTO substrates into a aqueous potassium phosphate solution at pH 7 containing Co^{2+} and TM ions from dissolved nitrate precursors and maintaining a certain potential for at least 1 h utilizing a three electrode setup with a Gamry Reference 600 workstation.

While the high DP batch has been prepared in a single compartment electrochemical cell, an H-cell was used for the low DP batch. Here, the cathode (counter electrode) was kept in a P$_i$ buffer solution containing compartment, which was separated by a porous frit from the anode (working electrode) compartment filled with a TM ion containing P$_i$ solution. A Pt wire was used as the counter electrode and a Ag/AgCl electrode was used as reference. All potentials in this report are given in reference to the normal hydrogen electrode (NHE) if not stated otherwise. The potential given by the reference electrode, E(Ag/AgCl), has been converted to the more common NHE potential according to $E(\text{NHE}) = E(\text{Ag/AgCl}) + 0.197$ V, where we have not subtracted the iR-drop in the electrolyte.

Fig. 1(a) shows cyclic voltammetries (CV's) of blank FTO substrates exposed to the different ion solutions recorded at 50 mV/s, demonstrating that catalytic activity already occurs during film formation when the TM ions are still in solution. At low potentials, i.e. 1.3 V vs. NHE, the solution containing only Co^{2+} shows the highest current density, but is surpassed by the hybrid solutions at higher potentials. During electrodeposition, i.e. film formation, the current density through the FTO substrates gradually increases with time as shown in Fig. 1(b) for the various solutions at a low DP of 1.3 V vs. NHE. Our findings for the pure Co-P$_i$-films are similar to those of Kanan and Nocera [2]. All deposition processes are associated with an OER, indicated by bubble formation on the working electrode. For all solutions the films show catalytic enhancement of the deposition process after a short initial stabilization. Pure Co^{2+}-ion solutions show the highest efficiency for the OER, followed by the Mn^{2+}Co^{2+}-hybrid solution. Similar results were obtained for the high DP samples.

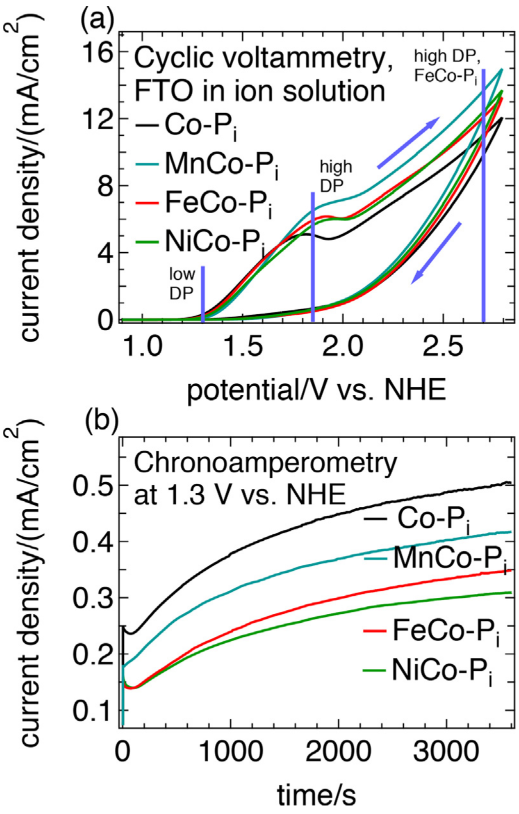

Fig. 1. (a) Cyclic voltammetry of blank FTO substrates in respective ion solutions. (b) Chronoamperometry of FTO substrates in the various solutions during deposition at low DP of 1.3 V vs. NHE.

In order to determine the electrochemical properties of the films a CV was carried out on duplicates of all low DP films in a P$_i$ buffer solution without TM-ions. Here, the currents collected by the working electrode have been recorded while its potential was gradually increased from 0 to 1.4 V vs. NHE and back to 0 at a rate of 1 mV/s. Visible bubbles started to form shortly before reaching 1.3 V vs. NHE. Fig. 2 shows CV's of the low DP films. Here, in the absence of TM-ions in the solutions, the Co-P$_i$-film shows the highest efficiency for OER followed by FeCo-P$_i$ and MnCo-P$_i$. The respective overpotentials for the OER are summarized in Table 1.

All samples were prepared ex situ approximately one to two weeks before transportation to the synchrotron. These types of samples have been shown [10] to be stable in ambient conditions in the bulk (for effects in surface vicinity see below). This notwithstanding, all samples were carefully stored in closed containers. Additionally, a subset of similar test samples that were prepared on site, a few hours or minutes prior to insertion to the vacuum chamber for performing synchrotron measurements corroborates this assertion by showing similar results.

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