Characterisation of a water-oxidizing Co-film by XAFS

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Abstract. A major enterprise for scientists worldwide is the search for alternative fuels and molecular hydrogen (H₂) is a promising candidate. Its large-scale technical production needs to involve water-oxidation catalysts from inexpensive and abundant materials. Here, a water-oxidizing Co-based catalyst film (CoCF) is investigated. We review and extend our previous X-ray absorption spectroscopy (XAS) measurements (at Helmholtz-Zentrum Berlin/BESSY) by comparison to LiCoO₂, a Co³⁺ compound of similar structure and composition. Further evidence is presented that the bulk oxidation state of cobalt in the CoCF is 3⁺. We propose that the catalyst film is composed of interconnected complete and/or incomplete Co-oxo cubanes possibly forming a disordered network of the basic Co₃/₄(µ-O)₄ units.

1. Introduction
The large-scale production of molecular hydrogen (H₂) from water requires the use of efficient water-oxidation catalysts based on inexpensive and abundant materials. Recently, several new transition-metal complexes for homogeneous catalysis of water oxidation have been described; rare metals have been typically employed [1, 2]. A cobalt catalyst for electrochemical water oxidation reported by Kanan and Nocera [3] has attracted much interest because of its efficiency at neutral pH and self-assembly from low-cost materials. This catalyst assembles as an amorphous layer on inert cathodes by electrodeposition starting from an aqueous solution of simple cobalt and phosphate salts. The resulting cobalt catalyst film (CoCF) also contains phosphate and potassium (or sodium) [4]. Self-repair of the film has been reported [5]. It is noteworthy that there may be similarities with respect to oxidative self-assembly and function between the CoCF and the protein-bound Mn₄Ca(µ-O)₆ complex facilitating efficient water oxidation in photosynthesis [3, 6-10].

Previously, we have reported findings on the oxidation state and proposed structural elements for the CoCF [11]. Here, we review and extend our X-ray absorption spectroscopy (XAS) measurements by comparison to another Co³⁺ compound of similar composition, namely LiCoO₂.

2. Experimental
The Co-film on indium tin oxide (ITO) was formed by cathodic electrodeposition from an aqueous solution of KH₂PO₄ and K₂HPO₄ (pH 7) containing [Co(OH₂)₆](NO₃)₂, with concentrations of 0.1 M PO₄ and 0.5 mM Co²⁺. A voltage of 1.4 V (vs NHE) was applied during film formation. The LiCoO₂ powder was diluted (1:17 w/w) with boron nitride (BN). Further details of the preparation are described in [11]. The atomic structure of the LiCoO₂ powder is known from crystallography [12].

The cobalt K-edge measurements were performed at the KMC-1 bending-magnet beamline [13] of the Helmholtz-Zentrum Berlin for Materials and Energy (formerly BESSY II, Berlin) using a double-
crystal monochromator (Si-111, scan range of 7600-8700 eV). The samples were kept at 20 K (liquid He cryostat). The X-ray fluorescence of the CoCF samples was either detected by a photodiode, which was shielded against scattered incident X-rays by an iron foil (10 μm), or by an energy-resolving solid-state detector. Ion chambers were employed to detect the intensity of the incoming X-rays ($I_0$), the X-rays going through the sample ($I_1$), and the X-rays passing an energy standard ($I_2$) placed between the $I_1$ and $I_2$ chambers. The LiCoO$_2$ sample was measured in transmission mode. The K-edge inflection point at 7709 eV of a simultaneously measured Co metal foil was used for calibration of the energy axis. For conversion of the energy axis to a k-vector axis, an $E_0$ of 7710 eV was used. No indications for radiation-induced modifications of structure or oxidation state were detected.

![Figure 1. Co K-edge XANES spectra of a catalyst film sample (CoCF) and reference samples with oxidation state 3+ (LiCoO$_2$) and 2+ ([Co(OH)$_2$)$_6$(NO$_3$)$_2$). The CoCF spectrum was acquired in fluorescence mode and the reference spectra in transmission mode.](image)

### 3. Results & Discussion

The XANES spectra of CoCF and LiCo$^{III}$O$_2$, a material of known structure [12], are compared in figure 1. The spectra of both samples are the average of 6 scans normalized as reported in [14]. The edge positions as defined by the half-height of the normalized edge jump were found to be 7720.5±0.2 eV (LiCo$^{III}$O$_2$) and 7720.7±0.2 eV (CoCF). (Note that in [11], erroneously, an incorrect value of 7717.5 eV was given for the CoCF edge position.) The integral method [15] with limits of 0.15<μ<1.0 yielded 7721.2±0.1 eV (LiCoO$_2$) and 7721.0±0.2 eV (CoCF). We refrained from employing the inflection point method which here is inappropriate due to a shoulder in the LiCoO$_2$ spectrum [14]. In general, the spectra of both samples are very similar; subtle differences may arise from the higher crystallinity of LiCoO$_2$. The nearly perfect identity of the edge positions as well as the similarity in the XANES suggests identical oxidation state and similar coordination geometry. Thus, we conclude that octahedral coordination of Co$^{III}$ by six oxygen ligands likely prevails in the CoCF.

The Fourier-transformed EXAFS spectra of the CoCF and LiCoO$_2$ samples are shown in figure 2. The parameters of the spectral simulations obtained by curve-fitting are given in table 1. Identical amplitude and phase functions obtained from FEFF8.4 [16, 17] were used for both spectra in the fit process. The known coordination numbers of the LiCoO$_2$ reference were fixed, in order to obtain estimates of the (correlated) Debye-Waller parameter ($\sigma$). For the 5.6 Å interaction, the same $\sigma$ was used in the simulation of both compounds, which allowed us to obtain a refined estimate of the CoCF’s coordination number. The value of 0.4 Co atoms reported here is about half of the value previously reported [11] for this distance.
Figure 2. Fourier-transform (FT) of an EXAFS spectrum of the catalyst film (CoCF) and crystalline LiCoO$_2$ which has the same octahedral Co building blocks, but those blocks are arranged in an extended layer of side-sharing Co$^3$O$_6$ octahedra, which can be viewed also as a layer of side-sharing, incomplete Co-oxo cubanes (Co(µ-O)$_4$). The positions of the peak maxima are highly similar, confirming the existence of Co-Co distances of 2.8 at 5.6 Å in the CoCF. For the FT of the $k^3$-weighted EXAFS oscillations, a $\cos^2$ window function covering the complete $k$ range (2-14 Å$^{-1}$) was used, thereby ensuring complete suppression of sidelobe artefacts.

Figure 3. Drawing of the proposed structural motif deduced from XAS data for the bulk of the CoCF (cobalt in black, oxygen in grey). The catalytic film could be composed of a mixture of complete and incomplete cubanes. The ratio of 1:1 is shown for illustration purposes only. It is not excluded that the CoCF material contains exclusively interconnected complete Co$_4$(µ-O)$_4$ cubanes or exclusively incomplete Co$_3$(µ-O)$_4$ cubanes. In the latter case, the extent of edge-sharing between cubanes needs to be higher, in order to account for the presence of 4±1 Co-Co vectors of 2.8 Å length (per X-ray absorbing Co).

Table 1. Parameters for the EXAFS simulation in figure 2.

| Atoms  | CoCF  | LiCoO$_2$ |
|--------|-------|-----------|
|        | N     | R (Å)     | σ ($10^3$Å) | N     | R (Å)     | σ ($10^3$Å) |
| Co-O   | 5.7   | 1.89      | 51          | 6*    | 1.91      | 60          |
| Co-Co  | 4.1   | 2.81      | 69          | 6*    | 2.81      | 49          |
| Co-Co  | -     | -         | -           | 6*    | 4.94      | 51          |
| Co-Co  | 0.4   | 5.61      | 28*         | 6*    | 5.61      | 28          |

The parameters marked by an asterisk were fixed; all other parameters were determined by curve-fitting of the data ($k$ range 3-12 Å$^{-1}$). In both simulations, the amplitude reduction factor $S_0^2$ was 0.7 and the energy axis of the fit was shifted by +1.54 eV relative to the initially selected $E_0$ of 7710 eV. The coordination numbers N of the LiCoO$_2$ simulation were fixed to the known values [12].
The distances of 1.9 Å and 2.8 Å determined by EXAFS fits are very similar in both compounds, indicating that they share a common structural motif: Co$^{III}$ octahedrally ligated by 6 oxygen atoms and interconnected by di-µ-oxo bridges in the way shown in figure 3. The high coordination number suggests that Co-(µ-O)$_2$-Co units are interconnected, inter alia resulting in a Co-Co distance of 5.6 Å (figure 3). The corresponding FT peak is much more pronounced in LiCoO$_2$ indicating a low extent of long-range order in the CoCF (compare also the magnitude of the corresponding coordination numbers in table 1).

We emphasize that figure 3 shows an artwork of the proposed bulk structure of the CoCF catalyst, illustrating the possible presence of complete and/or incomplete cubanes as deduced from the XAS analysis. Further interconnections of the shown building blocks may result in an extended, but overall highly disordered network of complete and/or incomplete cubanes.

4. Summary

We have provided further evidence for the previously proposed structural building blocks in the water-oxidizing CoCF, i.e. interconnected complete or incomplete Co$^{III}$-oxo cubanes. This was achieved by comparing the CoCF to a micro-crystalline reference sample, LiCoO$_2$, for which the structure is known at the atomic level. This comparison also confirms that in the CoCF limited long-range order is present, but this order is low as indicated by the roughly ten times weaker 5.6 Å EXAFS interactions (in comparison to LiCoO$_2$) and by the absence of a 4.9 Å peak resolved in the FT. Comparison of the XANES spectra strongly supports that the bulk oxidation state of Co in the CoCF is 3+ (Co$^{III}$).

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