Tunable pH-dependent oxygen evolution activity of strontium cobaltite thin films for electrochemical water splitting

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Understanding the oxygen evolution reaction (OER) dependence on the reaction environment pH is important to define an optimal pH value for high electrocatalytic activity. SrCoO$_2.5$ (SCO) films with the brownmillerite (BM) phase (Fig.1(a)) are investigated for their strain effects on the OER activity, with particular regard to the pH dependence. Pulsed laser deposited films on (100) LaAlO$_3$ substrates with different thicknesses (25, 50 and 100 nm) and, thus, different compressive strain conditions, are characterized in terms of long range and near-order structural properties and electrochemical OER activity. By comparison, more strained thinner films have smaller OER current at lower pH conditions, but higher sensitivity to the environment pH (Fig.1(b)). Spectroscopic measurements allow us to correlate such behaviors to the Co 3$d$–O 2$p$ hybridization effects of the CoO$_6$ octahedral sites, which lead to a variation of the 3$d$ level electronic occupation. In particular, x-ray absorption (XAS) measurements of Fig.1 (c), after background subtraction, reveal the higher XAS pre-edge for the thinner strained films, indicating a greater number of hybridized empty states with respect to the thicker films. At the same time, density functional theory (DFT) calculations (Fig.1(d)) show that the oxygen vacancy channels of the CoO$_4$ tetrahedral sites are stable with respect to the strain effects. We demonstrate that the compressively strained BM-SCO films allow the tuning of the OER properties by varying the stress field. These results provide new perspectives to manipulate the pH dependent OER activity, useful for designing water splitting-based devices with optimized performances.

Fig.1. (a) BM structure. (b) Current density of the 25, 50, and 100 nm BM-SCO films at 1.75 V versus reversible hydrogen electrode after iR correction in O$_2$-saturated moles of KOH (potassium hydroxide) dissolved in 1000 cm$^3$ of distilled water: 0.1 M KOH (pH 13), 0.3 M KOH (pH 13.5) and 1.0 M KOH (pH 14). (c) O K-edge XAS curves of BM-SCO films with different thickness in total electron yield. The solid black lines are the background curves. The inset shows the zoomed background-subtracted O 2$p$–Co 3$d$ hybridization pre-edge region of the spectra. (d) Oxygen vacancy formation energy calculated with a v2 x v2 x v2 supercell at different oxygen ion positions compared with the results for perovskite-SCO reported by H. A. Tahini et al. ACS Catal., 2016, 6, 5565.