Towards quantitative correlation of surface reconstruction and/or reduction of perovskite catalysts simultaneously by ELNES

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Water splitting aided by perovskite catalysts has been attracting a lot of attention both for the oxygen reduction and for the oxygen evolution reactions. [1,2]. The structure and absorption sites of the surfaces of the oxides are thought to be of critical importance for their catalytic performance. A lot of theoretical approaches have been published on the potential effect of the catalyst morphology for optimum water splitting but few experimental studies exist to confirm the theoretical results. Electron energy loss spectroscopy (EELS) is a promising technique since it can probe the fine structure of transition metal edges and provides information on the coordination number and oxidation state of the surfaces of the perovskites. However, interpretation of the results requires standards as well as theoretical predictions of the shape and position of the EEL spectra.

To determine whether through EEL spectra we can deduct complementary information of the surface reconstruction, i.e. coordination number, and/or oxidation state of perovskite catalysis, we collected high energy resolution energy loss near edge structure (ELNES) data from a highly active and complex catalyst for the oxygen reduction reaction, lanthanum manganese. $LaMnO_3$ is a Jahn-Teller distorted orthorhombic crystal that absorbs O_2 on its surfaces and it is very stable under electron beam irradiation at high accelerating voltages [3]. Core-loss EELS provides information on the energy dependence of the density of empty states in the conduction band and is similar to x-ray absorption spectroscopy. Therefore, for the interpretation of the spectroscopy results, we apply three different theoretical modules developed for x-ray or/and electron spectroscopies: Quantum Espresso, FDMNES, and an in-house code based on the Crystal code that provides information of the probability of the transitions as well. It was previously shown that a non-negligible contribution of local coordination, suggesting a surface reconstruction, can be correlated with the observed ELNES of the Mn $L_{3,2}$ edge [4]. Herein, the O K edge is also investigated towards furthering our understanding of the surface properties that need to be optimized for the complex oxides that exhibit excellent potential for renewable energy applications.

References

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