Activation of MnO_2 Catalysts by Mn^{3+} Ions

The conversion of water to H_2 and O_2 is one of the most energy dense carbon-neutral fuel schemes to store solar energy [*1*]. Effective catalysts for the oxygen evolution reaction (OER) require a design that manages the coupling of electrons and protons so as to avoid high energy intermediates and provide high stability and performance in various media. Manganese oxide films are desirable oxygen evolution reaction (OER) catalysts due to their stability in acidic solutions and viability as earth-abundant materials. Enhanced catalytic activity of MnO_2 incorporated with Mn^{3+} provides an imperative for understanding the structural and electronic effects giving rise to the superior OER catalysis.

Researchers from the “Center for Next Generation Materials by Design” EFRC sought to study the phenomenon and role of Mn^{3+} in MnO_2 films. Mn^{3+} ions may be introduced electrochemically by using the comproportionation of MnO_2 with $Mn(OH)_2$ to produce a hausmannite-like intermediate (α-Mn_3O_4) [*2*]. Subsequent electrodeposition of birnessite *via* the hausmannite intermediate creates a uniquely active surface for OER.

The resultant activated films (denoted δ-MnO_2^{act}) exhibit orders of magnitude higher OER activity. Figure 1 shows the cyclic voltammograms of as-deposited δ-MnO_2 and activated films over a potential window that includes OER activity and/or film activation. Several notable features are observed. Figure 1a shows the CV for the OER activity of δ-MnO_2 in the absence of Mn^{3+} incorporation. Wave A corresponds to the nucleation and deposition of δ-MnO_2 and Wave B corresponds to the modest OER activity of birnessite. Figure 1b shows the CV for the OER activity of films before and after Mn^{3+} incorporation. Under cathodic potentials NO_3^- is reduced, forming hydroxide anions at the electrode surface, thus driving the production of $Mn(OH)_2$ and enabling comproportionation to occur. After inducing the comproportionation reaction upon cathodic scanning, the return trace shows a significant increase in current associated with OER (wave D). The experiments in Figure 1 taken together establish that δ-MnO_2 alone shows only modest OER activity, regardless of potential cycling of the film and only when Mn^{3+} is introduced, is enhanced OER activity observed.

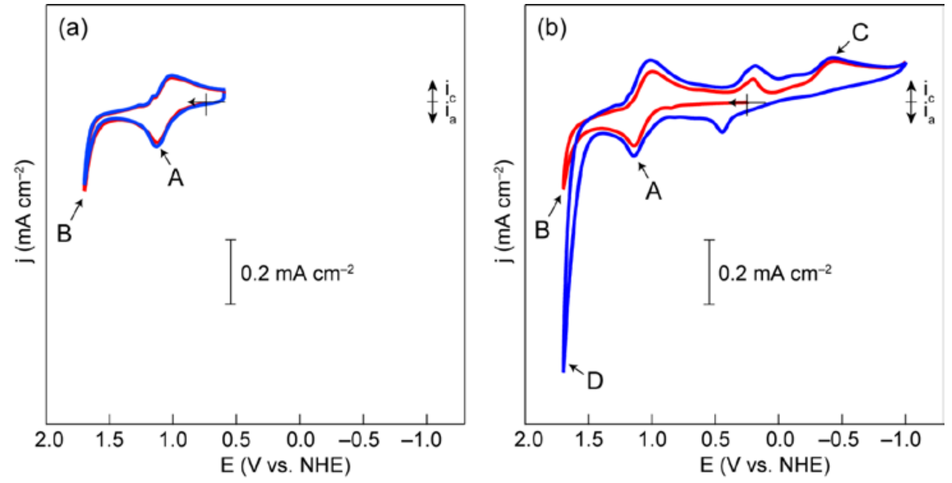

Figure 1: Cyclic voltammograms of a 1 cm^2 FTO electrode in 0.5 mM Mn^{2+} and 0.9 M KNO_3 solution at 100 mV/s scan rate showing the first (red ▬) and second (blue ▬) cycles, for the (a) as-deposited δ-MnO_2 and (b) the as-deposited film activated via the incorporation of Mn^{3+} ions by the comproportionation reaction. Reprinted with permission from Morgan Chan *et al*. 2018, *PNAS*, DOI: 10.1073/pnas.1722235115.

In-situ x-ray absorption spectroscopy measurements made during the electroactivation of electrochemically deposited δ-MnO_2 phase show that Mn^{3+} character remains present in OER active catalyst films and that the Mn–O bond coordination number is lowered with the formation of Mn^{3+}. Figure 2 shows the *in situ* XANES spectra collected on an as-deposited δ-MnO_2 (birnessite) film activated by applying a two-step potential alternately between 1.1 V and –0.4 V. The δ-MnO_2 film was electrodeposited in the *in situ* x-ray cell during XAS data collection. Following each multi-step cycle, an XAS spectrum was recorded. The energy of the edge shifts to lower energy upon the application of the first multi-step potential consistent with the generation of Mn^{3+}. Moreover, sequential spectra of cycles ending at the cathodic limiting potential exhibit a lower energy absorption threshold than those terminating with the anodic limiting potential, giving rise to the sawtooth pattern shown in the inset. Subsequent cycles ultimately converge to an absorption threshold of 6549.75 to 6550.0 eV, consistent with a lower average oxidation state of manganese in activated films as compared to the as-deposited film. The indication of a lower oxidation state in Figure S6 is consistent with the lower average oxidations state of +3.6–3.8 measured previously by coulometry [2] and CV and XPS studies [3,4].

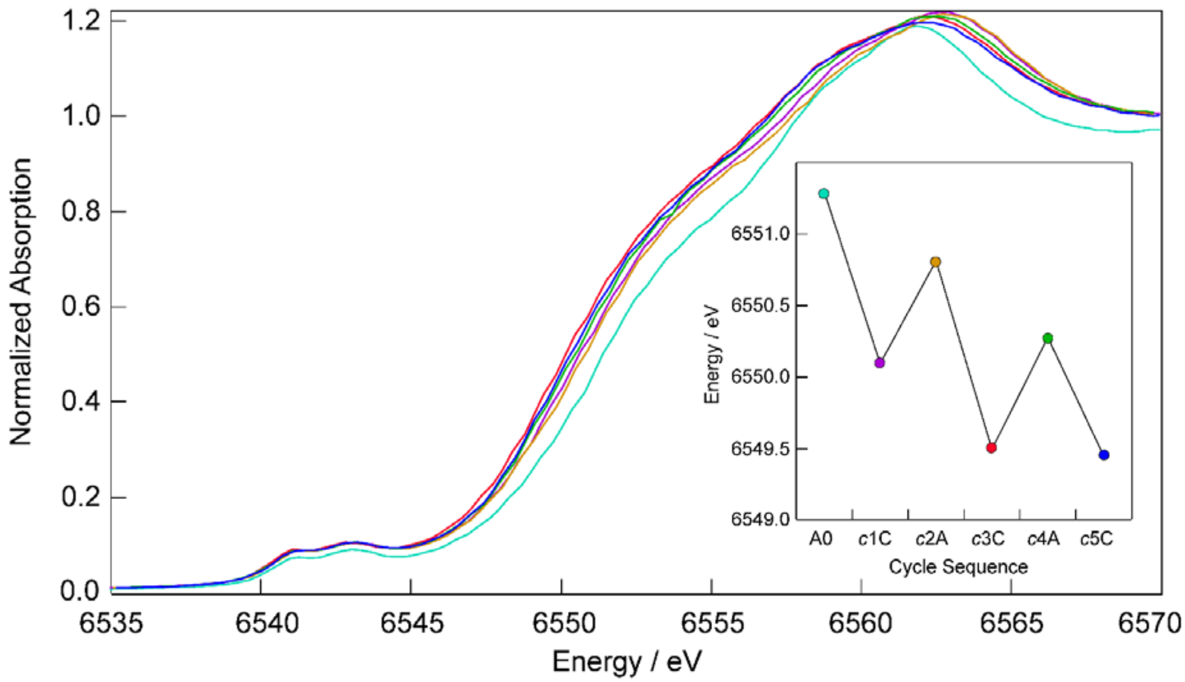

Figure 2: *In situ* XANES spectra of an as-deposited δ-MnO_2 film subject to multipotential step activation. XANES spectra were collected after applying a potential between 1.1 V and –0.4 V 25 times with a cycle terminating at the anodic or cathodic potential. One cycle (designated *c*) = 25 steps. The cycle number is designated numerically, and A and C denote a cycle terminating at an anodic or cathodic potential, respectively. The inset shows the energy position of the XANES edge determined from the inflection point as deduced from the maximum of the first derivative. The edge positions in the inset are color-coded to match the XANES spectra for cycles A0 (▬), *c*1C (▬), *c*2A (▬), *c*3C(▬), *c*4A (▬), and *c*5C (▬). Reprinted with permission from Morgan Chan et al. 2018, PNAS, DOI: 10.1073/pnas.1722235115.

Computational studies, supported by EXAFS results, reveal that during the electrochemical activation the Mn^{3+} ions are trapped in a tetrahedral environment, which is kinetically stable and induces local strain of the lattice, which is observed in Raman microspectroscopic spectra. This strain results in a raising of the O2p valence band above the Mn^{3+} tetrahedral (T_d) and Mn^{4+} octahedral (O_h) valence bands with a commensurate lowering of the metal-based conduction bands. Oxidation of tetrahedral Mn^{3+} is thus more difficult than that of oxygen. The induced local strain on the oxide sublattice leads to a reduced HOMO-LUMO gap. The confluence of a reduced HOMO–LUMO gap and an oxygen- based HOMO facilitates OER in Mn^{3+}-incorporated MnO_2 catalyst films.

The researchers show that (i) Mn^{3+} is stabilized kinetically in tetrahedral sites and (ii) its presence strains the oxide lattice leading to a favorable disposition of oxide-based versus metal-based energy levels that favors enhanced OER activity. The studies conducted rationalize why Mn^{3+} is observed to persist at the onset of OER in MnO_2 polymorphs, why the presence of Mn^{3+} enhances OER catalysis, and offer a new design concept of exploiting ion-induced lattice strain for creating superior metal-oxide OER catalysts.

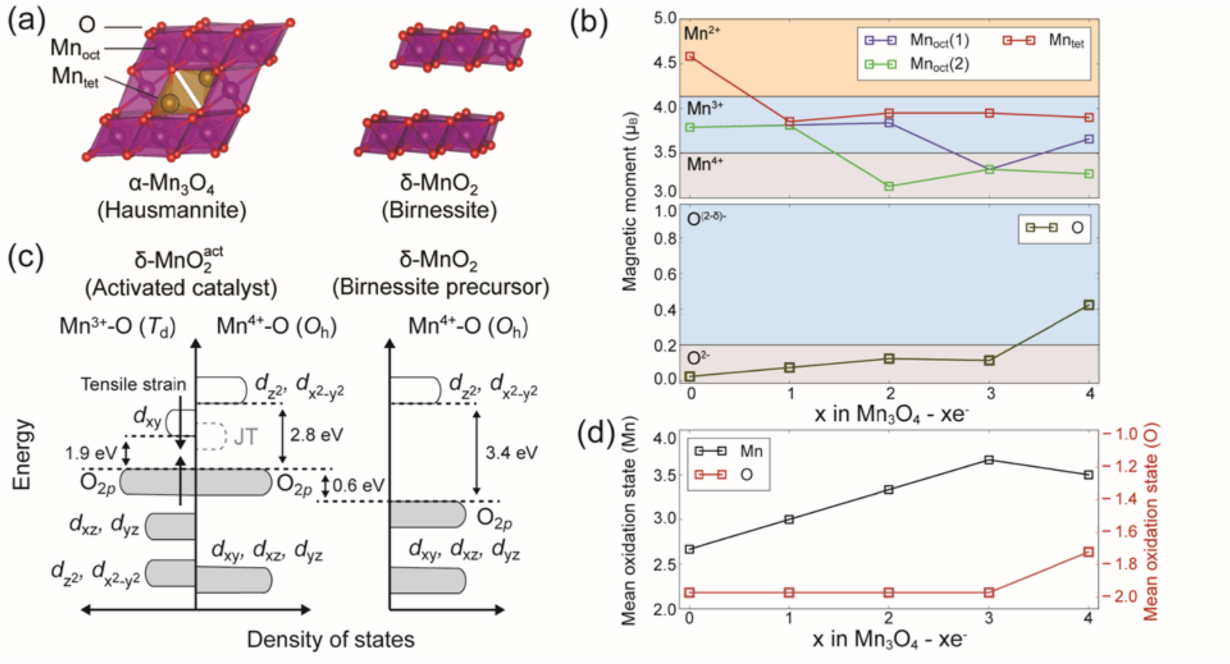

Figure 3: Electronic structure of the activated catalyst, based on an oxidized α-Mn_3O_4 hausmannite structure as a model system containing both octahedral and tetrahedral Mn–O environments. (a) Schematic representation of the α-Mn_3O_4 hausmannite and δ-MnO_2 structures, illustrating their common underlying face-centered-cubic oxygen framework, and similarity in octahedral Mn structure. The unique tetrahedral Mn sites in α-Mn_3O_4 are highlighted. (b) Evolution of oxidation states of Mn and O as electrons are removed from the α-Mn_3O_4 model system. Oxidation states are derived from the values of characteristic atom-projected magnetic moments according to typical values observed for computed manganese oxides and hydroxides. (c) Schematic of the band structure of the activated catalyst system, derived from the "α-Mn_3O_4– $3e^-$" model. The T_d and O_h sections of the band diagram represent tetrahedral and octahedral Mn environments, while the Jahn-Teller orbital depicts the relative position of the O_h LUMO accounting for structural relaxation through Jahn-Teller distortion. (d) Average valence of Mn and O as a function of oxidation level, as indicated by the electronically-titrated α-Mn_3O_4 model. Reprinted with permission from Morgan Chan *et al*. 2018, *PNAS*, DOI: 10.1073/pnas.1722235115.

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