Modulating the O-binding Energies of Mn-based Perovskites to Maximize Solar Thermochemical Hydrogen Production

Jamie A. Trindell1, Nicholas A. Strange2, Sarah Shulda3, Robert T. Bell3, Tadashi Ogitsu4, Anthony McDaniel1 and Joshua D. Sugar1

[1.] Sandia National Laboratories, Livermore, California, USA.
[2.] SLAC National Accelerator Laboratory, Menlo Park, California, USA.
[3.] National Renewable Energy Laboratory, Golden, Colorado, USA.
[4.] Lawrence Livermore National Laboratory, Livermore, California, USA.

Solar thermochemical hydrogen (STCH) production is a promising method for the clean evolution of H_2 from H_2O and solar thermal energy through a two-step redox cycle. In the first step, a transition metal oxide (TMO) is thermally reduced, releasing O_2 from the crystal lattice and subsequently forming oxygen vacancies (O_v). In the second step of a STCH cycle, the metal oxide is thermally oxidized in steam, resulting in re-occupation of O_v and forming H_2 gas as a product. During this redox cycle, the formation of O_v in the crystal lattice of the TMO are stabilized by the ability of the transition metal to adopt different valence states. For example, manganese is well known for its ability to change oxidation states between $Mn^{4+}/Mn^{3+}/Mn^{2+}$ during redox cycling. While Mn-based perovskites have been reported as promising materials for STCH production, little mechanistic insight into how to further improve on the overall H_2 production in these systems is known. Ideally, modulating the Mn-O binding energy in a complex metal oxide or perovskite would enable optimization of both O_v formation, enhanced by low binding energies, and re-oxidation by steam, enhanced by high binding energies. Striking the correct balance between these two redox steps will require improved insight into the mechanism relating Mn-O binding environment and oxidation state to O_v formation energetics.

Here we explore two modifications of local Mn-O environments in the Mn-based perovskite $BaCe_{0.25}Mn_{0.75}O_3$ (BCM), a highly performance material for STCH production. First, the formation of twin defects during redox cycling in BCM creates local chemical environments that modify the O_v formation energy. The structure of these twins, imaged using high-resolution scanning transmission electron microscopy (STEM), and the corresponding O_v formation energies, calculated from density functional theory (DFT), are shown in Figure 1 for BCM. We propose a mechanistic pathway by which twin domains provide nucleation sites for phase transformations that affect the overall water-splitting activity observed in these systems. Second, substitution of other cations onto the neighboring Ce sites of BCM, a family of related of $BaX_{0.25}Mn_{0.75}O_3$ (BXM) materials, where X = Pr or Nb, further modifies the local Mn-O environment in this system. While these substitutions resulted in BXM materials with matching structure to BCM (Figure 2), stagnation flow reactor tests of their H_2 production demonstrate a strong influence of X on performance. Interestingly, BCM demonstrated the highest H_2 production activity, especially under high conversion conditions ($H_2O:H_2$ 1333:1) compared to both BNM and BPM. Combining information obtained from X-ray diffraction (XRD), X-ray absorption (XAS), and STEM-EELS analysis we probed the compositional, structural, and electronic changes that occurred in these materials during redox cycling. Material was analyzed ex situ after STCH cycling in the flow reactor. and during in situ high-temperature reduction in the TEM. The H_2 production in this class of BXM materials depends on both the chemical environment and density of twin boundaries present during STCH cycling. High energy- and spatial-resolution microscopy are necessary to enable

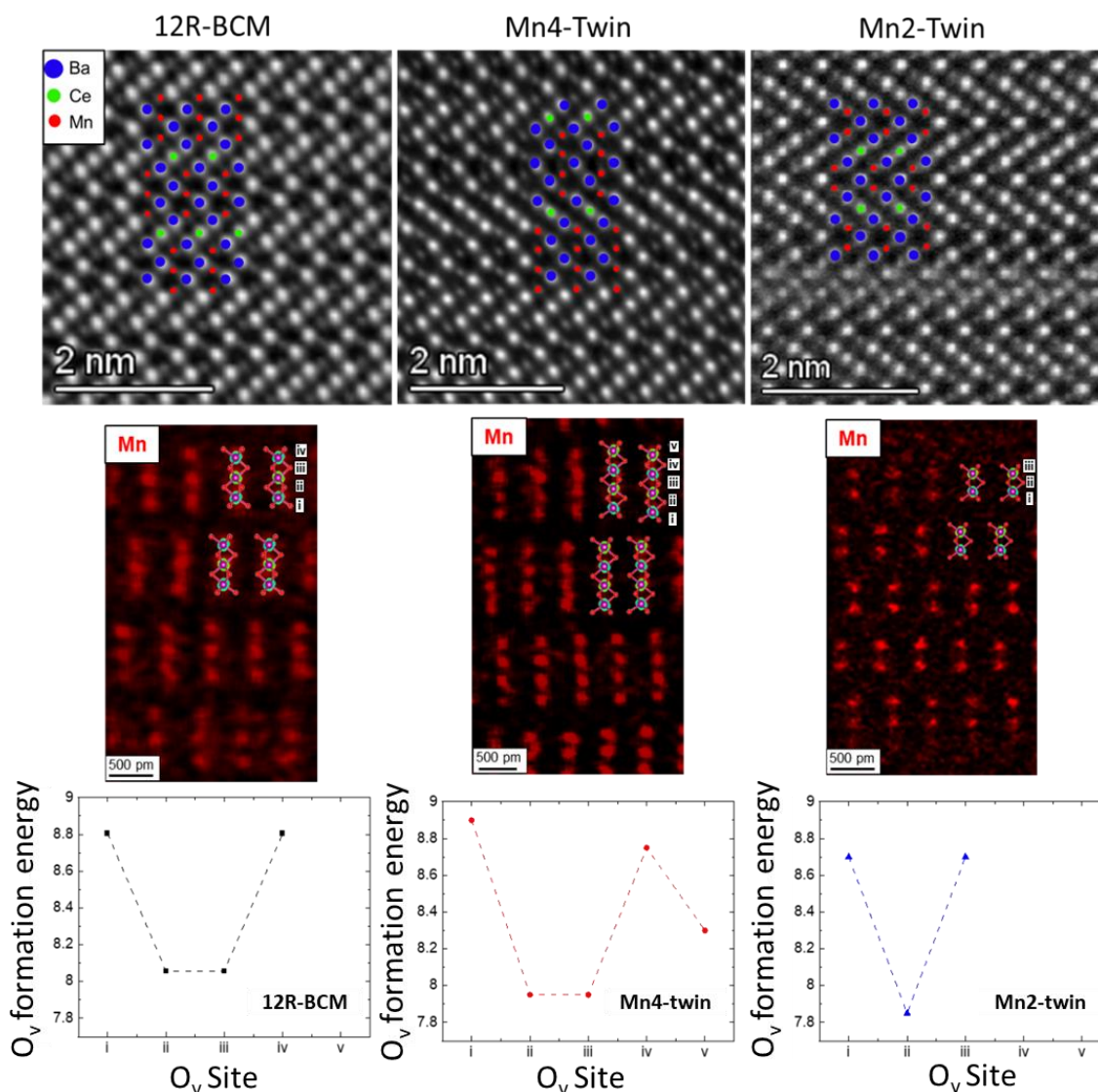observations of the microstructural features important for renewable energy production in these materials [1].

Figure 1. (top row) Atomic-resolution STEM images and structural model overlays, (middle row) EDS maps of the Mn-signal with structural model overlays (including O) of the Mn trimers, quadrimers, and dimers and (bottom row) scatter plots of the relative O_v formation energies of each of the O-binding sites designated in the EDS maps as i-v of (left column) 12R-BCM , (middle column) Mn4-twins, and (right column) Mn2-twins. 12R-BCM and the Mn4-twins are present in oxidized BCM while the Mn2-twin is present in the reduced state.
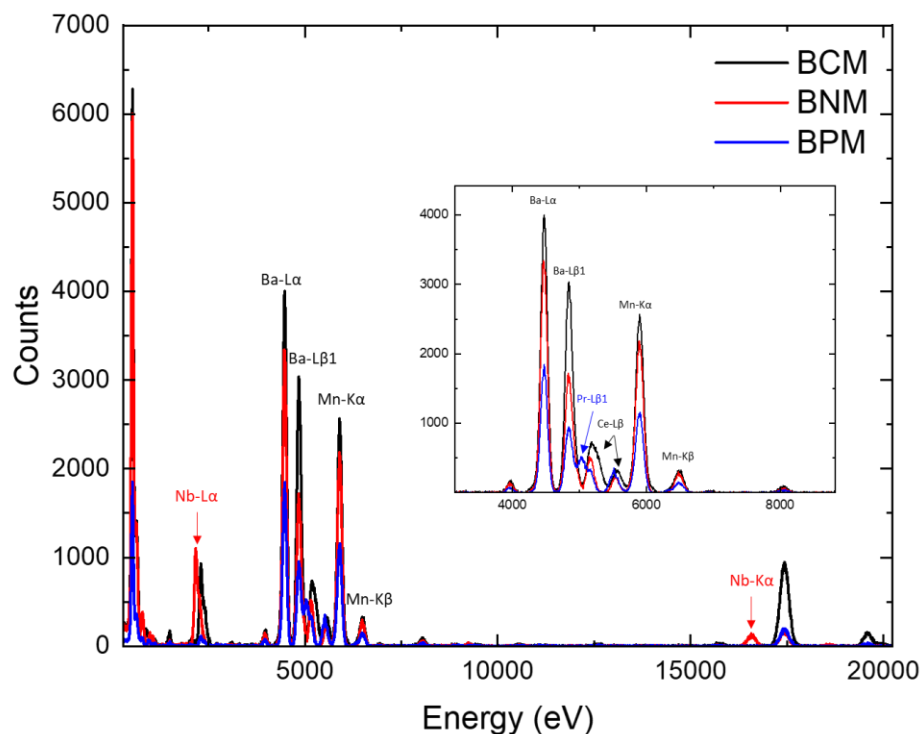
Figure 2. Energy dispersive X-ray (EDX) spectra of BCM, BNM, and BPM with corresponding elemental compositions for O, Ba, X (Ce, Nb, or Pr, respectively), and Mn in atomic percent.

References: