

Microstructural Transformations of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ to nNano-layered Mn Oxide during Electrochemical Water Oxidation

Bahareh Deljoo^{1,2}, Alireza Shirazi Amin³, S. Esmael Balaghi⁴, Younes Mousazadeh⁴, Tahereh Jafari³, Mohammad Mahdi Najafpour⁵, Steven L. Suib^{2,3}, Mark Aindow^{1,2}

¹. Department of Materials Science and Engineering, University of Connecticut, Storrs, CT, USA

². Institute of Materials Science, University of Connecticut, Storrs, CT, USA

³. Department of Chemistry, University of Connecticut, Storrs, CT, USA

⁴. Young Researchers and Elite Club, Shiraz Branch, Islamic Azad University, Shiraz, Iran

⁵. Department of Chemistry, (IASBS), Zanjan, , Iran

Hydrogen produced from water splitting by electrolysis is very attractive as a renewable energy source to replace fossil fuels [1]. In the past three decades, the use of artificial photocatalytic systems for water splitting has proven to be a favorable way of producing hydrogen from renewable resources [2]. The oxidation of water to oxygen is the most challenging part of the water splitting reaction because of the thermodynamic and kinetic limitations [3]. In order to promote this reaction, a variety of different metal oxide compounds have been developed as water oxidizing catalysts, however many of these compounds suffer from severe drawbacks such as toxicity, price, and limited availability that have prevented their widespread application [4]. Among the candidate metal oxides, manganese oxide compounds have attracted significant attention, not only because they are stable and earth abundant, but also because they are cost efficient.

In this study $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (LSM) is investigated as the catalyst in the electrochemical water oxidizing reaction at a pH of around 7.0, which converts the LSM to nano-layered Mn oxides over extended reaction times. The electro-chemical cell used for this study consists of two-half cells, which use Pt working and counter electrodes. The Pt anode is placed in 50 mL LiClO_4 (0.1M) solution with 200 mg of LSM powder kept in suspension by continuous magnetic stirring. The Pt cathode is placed in 1.0M KCl solution. The two half-cells are connected by a salt bridge in a glass U-tube, containing 5% agar in an aqueous solution of KCl (1.0M). The two Pt electrodes were connected to an external DC source and a potential difference of 2 V was maintained between the half-cells. The LSM oxidized at the Pt anode during the electrochemical water oxidation via the convective-suspension-collision mechanism, which is based on reactions during individual nanoparticle collisions [5].

The LSM catalysts were characterized using a combination of XRD and electron microscopy techniques. FEG-SEM and HRTEM imaging was performed using an FEI Teneo LoVac SEM operating at 5 kV, and an FEI Talos F200X TEM/STEM operating at 200 kV, respectively. Representative data obtained from the unexposed catalyst are shown in Figure 1. The XRD data confirmed that the material was single-phase LSM, and the SEM and TEM images showed that the powders were agglomerates (>10 μm) of single-crystal LSM particles 0.5-3 μm in diameter. After three weeks' exposure in the water oxidation experiment, the XRD and electron microscopy data show that LSM had converted to nano-layered Mn oxides with no long-range order (Figure 2). Cyclic voltammetry experiments showed that there was an improvement in the catalytic properties of the material after the 3-week exposure. Thus, conversion of LSM to nano-layered manganese oxides enhances the catalytic activity of the material for the water oxidation reaction. Experiments to investigate the mechanism for this improvement are underway. [6]

References:

- [1] A. Indra, et al, *J. Photochem. Photobiol. B Biol.*, vol. **152**, pp. 156–161, 2015.
 [2] K. Maeda, *J. Photochem. Photobiol. C Photochem. Rev.*, vol. **12**, no. 4, pp. 237–268, 2011.
 [3] M. M. Najafpour, et al, *J. Photochem. Photobiol. B Biol.*, vol. **141**, pp. 247–252, 2014.
 [4] M. M. Najafpour, et al, *Photosynth. Res.*, vol. **126**, no. 2–3, pp. 477–487, 2015.
 [5] X. Xiao and A. J. Bard, “*J. Am. Chem. Soc.*”, vol. **129**, pp. 9610–9612, 2007.
 [6] These SEM/TEM studies were performed using the facilities in the UConn/FEI Center for Advanced Microscopy and Materials Analysis (CAMMA).

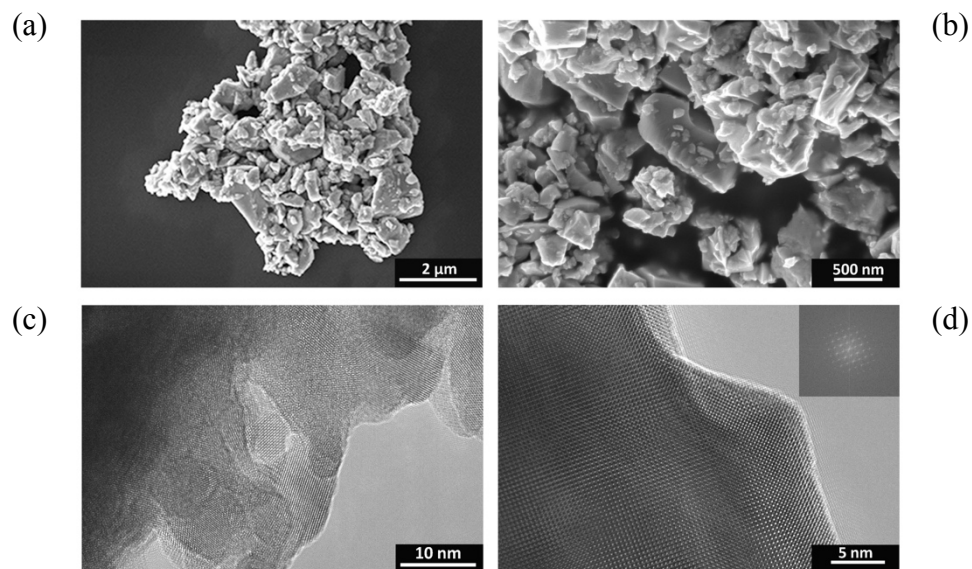


Figure 1. LSM catalyst prior to exposure: (a,b) SE SEM images; (c,d) HRTEM images.

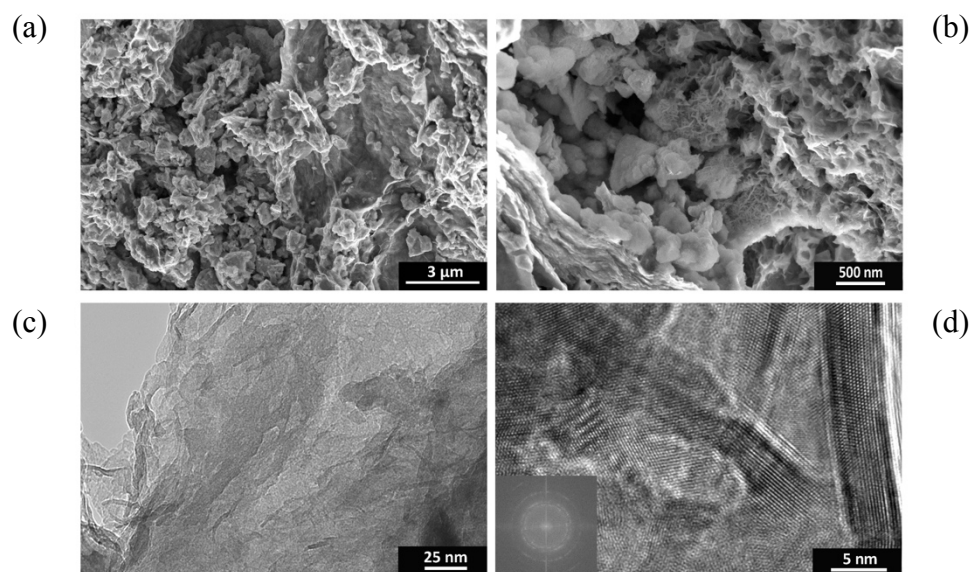


Figure 2. Nano-layered Mn oxides formed after 3 weeks' exposure in the water oxidation reaction: (a,b) SE SEM images; (c,d) HRTEM images.