
BESH2007 Nanostructured, Targeted Layered Metal Oxides as Active and Selective Heterogeneous Electrocatalysts for Oxygen Evolution

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Program Scope

The oxygen evolution reaction (OER) is an important chemical transformation that governs the performance of technologically relevant energy conversion and storage processes, such as electrochemical water splitting in electrolyzers and metal-air batteries. This reaction involves the evolution of oxygen gas from (i) oxygen ions formed from water splitting at high temperatures, (ii) oxygen containing species (i.e., OH^- , OOH^-) formed from water splitting at low temperatures, and (iii) metal-oxide discharge products (M_xO_2) in metal-air batteries. The main challenges to overcome in energy conversion via OER are expense (when catalyzed by noble metal-based electrocatalysts at low temperatures) and inadequate efficiency (when catalyzed by metal oxide based electrocatalysts at high temperatures). It has been shown that non-noble metal oxide electrocatalysts with layered structures, known as nickelate oxides, ($\text{A}_2\text{MO}_{4+\delta}$), that belong to the Ruddlesden-Popper first (R-P-1) series and comprise of alternating perovskite-like and rocksalt-like layers, exhibit promising OER activity.[1,2] We have recently demonstrated, the potential success of a bottom-up approach to design and synthesize lanthanum nickelate oxide (LNO) catalysts with optimal surface structure and surface oxygen exchange activity (process of exchanging lattice oxygen with gas-phase oxygen, which plays an important role in oxygen reduction and evolution on these materials).[3] Inspired by the ability to control the nanostructure of nickelate oxide materials and their high oxygen exchange properties, we proposed to explore the potential of nanostructured nickelate oxides as highly active electrocatalysts for oxygen evolution. Our objective is to combine quantum chemical density functional theory (DFT) calculations with well-controlled synthesis techniques and kinetic studies to develop structure–performance relationships that would enable the design of optimal nickelate oxide electrocatalysts for OER.

FY 2016 Highlights

We have employed DFT calculations, combined with experimental studies, to investigate the energetics associated with the surface oxygen exchange process on B-site modified LNO with well-defined nanostructures. Spin-polarized DFT calculations were performed using Vienna ab initio Simulation Package (VASP). A series of LNO materials with varying B-site compositions were studied, including La_2MnO_4 , La_2FeO_4 , $\text{La}_2\text{Ni}_{0.5}\text{Fe}_{0.5}\text{O}_4$, La_2CoO_4 , $\text{La}_2\text{Co}_{0.5}\text{Ni}_{0.5}\text{O}_4$ and La_2NiO_4 . We found that the surface chemistry of La_2NiO_4 can be tuned via substitution of the B (Ni) site. Our results showed that the binding energies of O on the transition metal site and O_2 on the surface O vacancy became gradually weaker as the B-site metal was varied from Mn to Fe, Co, and Ni. A volcano-type relationship between the calculated oxygen exchange rates and the binding energies for O_2 was found, suggesting that the binding energy of O_2 might be a good descriptor for identifying nickelate oxide materials with optimal activity. Furthermore, our calculations predicted that Co-doped LNO would lead to the highest activity for surface oxygen exchange when compared to the other nickelate oxides considered.

To support the computational predictions, a series of nanostructured B-site modified LNO ($\text{La}_2\text{Ni}_{0.868}\text{Co}_{0.132}\text{O}_{4+\delta}$, $\text{La}_2\text{Ni}_{0.838}\text{Cu}_{0.162}\text{O}_{4+\delta}$, $\text{La}_2\text{Ni}_{0.911}\text{Fe}_{0.089}\text{O}_{4+\delta}$) were synthesized using a reverse micro-emulsion method previously reported by our group for the synthesis of unmodified LNO nanorods selectively surface terminated predominantly by (001) NiO.[3] This synthesis method allows for control over the shape, morphology, and surface termination of nickelate oxides, which can be challenging to achieve using conventional solid state and citrate nitrate methods. Briefly, two separate quaternary reverse micro-emulsions each containing the surfactant cetyltrimethylammonium bromide (CTAB), water, hexane and n-Butanol were

prepared. In the first reverse micro-emulsion an appropriate amount of precipitating agent KOH was added, while in the second one the appropriate metal salts (La, Ni and dopant B site metal) were added. The two separate micro-emulsions were then mixed and stirred. The resulting gel was separated by centrifugation, washed, dried and calcined to yield the desired catalyst. We found that the ratio of water to the surfactant CTAB in the final mixed micro-emulsion played a critical role in obtaining the rod-shaped nanostructures.

Steady state kinetic isotopic exchange studies were utilized to determine the high temperature oxygen exchange kinetics on the nanostructured nickelate oxide catalysts with different compositions. Our experimental results showed that the trends were consistent with the theoretical predictions. For example, out of the catalysts tested, Co-doped LNO displayed the best performance for the surface oxygen exchange process. An approximate decrease of 25 kJ/mol in the activation energy for surface oxygen exchange was obtained on $\text{La}_2\text{Ni}_{0.868}\text{Co}_{0.132}\text{O}_{4+\delta}$ as compared to $\text{La}_2\text{NiO}_{4+\delta}$. [3] The kinetics of surface oxygen exchange on Fe and Cu doped LNO were also consistent with the DFT calculations. We are currently working on developing a microkinetic model for the oxygen exchange kinetics on these nickelate oxides to obtain additional insights into the reaction mechanism. Our future plan also involves determining the kinetics of low-temperature oxygen evolution on these nanostructured nickelate oxides in alkaline media using well-controlled rotating ring disk electrode studies. We anticipate that these studies will lead to structure–performance relationships that can be used to design optimal nickelate oxide catalyst for low and high-temperature OER.

References

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2. Das, A.; Xhafa, E.; Nikolla, E. Electro- and Thermal-Catalysis by Layered, First Series Ruddlesden – Popper Oxides. *Catal. Today* **2016**, Re-submitted after minor revision.
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