Nanostructure engineering of nickelate oxides for enhanced oxygen exchange and reduction kinetics

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Introduction
Surface structure of heterogeneous catalysts plays an important role in determining the activity and selectivity of many industrially relevant chemical processes.[1, 2] Controlling the nanostructure of complex metal-oxide based catalysts (such as perovskite and nickelate oxides) has been appreciably more challenging, and has mainly relied on utilization of thin film synthesis approaches,[3, 4] which lead to low surface area catalysts. Herein, we combine quantum chemical calculations along with controlled synthesis and kinetic studies to show that the surface structure of nickelate oxides plays an important role in oxygen exchange processes, and that synthesizing nickelate oxides with well-defined surface structure can lead to highly catalytically active catalysts for oxygen reduction. Oxygen reduction is a key chemical transformation that plays a critical role in many pertinent electrochemical energy conversion and storage systems (i.e., solid oxide fuel cells, electrolyzers and metal-air batteries). Nickelate oxides are layered, mixed ionic and electronic conducting materials that belong to Ruddlesden-Popper series containing alternating rocksalt-like and perovskite-like oxide layers. These materials have emerged as promising catalysts for oxygen reduction reaction due to their high oxygen exchange and transport properties. Our findings lay the groundwork for enhancing the catalytic activity of these complex oxide catalysts via engineering of their nanostructure.

Materials and Methods
Density functional theory (DFT) calculations were performed using Quantum ESPRESSO to determine the energetics associated with oxygen exchange on La2NiO4.125 (LNO) terminated by different facets. An effective Hubbard-like U parameter was added to the Hamiltonian to account for the localized d-orbital on-site Coulomb and exchange interactions. A microkinetic model was developed to calculate the rates of the oxygen exchange on LNO terminated with different facets. LaNiO4 nanocrystals with controlled surface structure were synthesized using a microemulsion method. Controlled kinetic studies if oxygen exchange on La2NiO4.14 were conducted using Steady State Isotopic Transient Kinetic Analysis (SSITKA) in a flow reactor. The electrochemical studies for oxygen reduction were conducted using anode-supported solid oxide fuel cells (SOFCs).

Results and Discussion
To identify the underlying factors that govern the oxygen exchange kinetics on nickelate oxides and potentially obtain insights on optimizing their surface reactivity toward oxygen reduction reaction, we have employed density functional theory (DFT) calculations to determine the energetics associate with this process on LNO terminated with different surface facets. Our calculations showed that the surface structure of LNO played an important role in their catalytic activity toward oxygen exchange (Figure 1a). We show that experimentally the distribution of the surface facet of LNO nanostructures can be tuned using a reverse microemulsion synthesis approach (Figure 1b). Our quantum chemical calculations combined with isotopic labeling kinetic experiments and electrochemical studies on SOFCs show that LNO catalysts with nanorod geometry exhibit higher rates for oxygen exchange and reduction as compared to LNO catalysts with spherical geometry (Figure 1c). Our results suggest that the enhanced activity of LNO nanorods is attributed to high fraction of (001) surface facets, which provide the best compromise of the energetics associated with two important steps in oxygen exchange/reduction - surface oxygen vacancies and dissociative adsorption of gas phase O2.

Significance
These results, for the first time, illustrate the impact of utilizing well-controlled nanostructures of mixed ionic and electronic conducting oxide electrocatalyst in enhancing the oxygen reduction kinetics in ceramic-based fuel cells. This is of significant importance since for many years the synthesis of mixed ionic/electronic oxide electrocatalysts for these systems has mainly relied on thermochemical and thin film fabrication approaches, which lead to low active surface area electrode electrocatalysts. With the advancements in the intermediate temperature solid oxide systems, design of electrode catalysts with controlled nanostructure will significantly impact their electrochemical efficiency.

Figure 1. a) DFT calculated rates for surface oxygen exchange on LNO terminated by different surface facets: (001), (100) and (111). (b) Scanning electron micrographs (SEMs) of LNO nanorods and nanospheres synthesized using a reverse microemulsion method. (c) Electrocatalytic performance (current density versus voltage and power density behavior) of SOFCs with LNO rods and spheres as cathode electrocatalysts.

References