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Understanding the spatial configurations of Sm_2O_3 in NiO interfaces Embedded-Loaded for Electrocatalytic OER process

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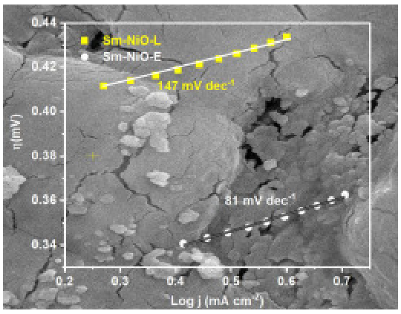
Abstract

The efficacy of the oxygen evolution reaction (OER) can be enhanced by adding samarium (Sm) species to electrocatalysts as was recently found. Significantly, the spatial dispersal of Sm substances in the NiO would define their individual aids to promote electrocatalytic activity, which in turn affects the accessibility of Sm substance as a dopant material. In this work, we perform in-depth studies of two different configurations of electrocatalyst, Sm_2O_3-embedded NiO (Sm-NiO-E) and Sm_2O_3-surface-loaded NiO (Sm-NiO-L), to investigate the consequence of their distinctive configuration on OER activity. The Sm-NiO-E electrocatalysts exhibit an overpotential (η) of 409 mV @ 10 mA cm^{-2} and a Tafel slope of 81 mV dec^{-1}, representing the advantage of the embedded design for water splitting in contrast to Sm-NiO-L (484 mV and 147 mV dec^{-1}). Embedding configuration exhibited the small-sized Sm_2O_3 clusters into the host for a bigger special interfacial region and enriching interfacial defects allows Sm-NiO-E to have a greater O_2 adsorption capability and better tuned electronic assemblies of the interfacial active region. These results provide a valuable guide for designing electrocatalysts with different spatial layouts to enhance their electrocatalytic properties.

Graphical abstract



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Introduction

The highly effective storage and conversion of power produced from renewable energies into big industrial stands remain a significant problem for sustainable energy usage, despite recent advancements in energy harvesting [1], [2], [3], [4]. Examples of efficient methods that enable sustainable storage and energy conversion include rechargeable metal-air batteries (Zn & Al-air) [5] and water electrolyser cells [6] catalysed by elements found in abundance on Earth. Besides this, the oxygen evolution reaction (OER) suffers from ineffective oxygen production owing to slow kinetics exhibiting a 4 e^- process, where substantial overpotentials are essential [7], [8], [9], [10], [11]. Both metal-air batteries and H_2O electrolysis with hydrogen evolution reaction (HER) involve the oxygen reduction process. Earth-abundant electrocatalysts including, transition metal-based catalyst has been modified using a variety of techniques to increase the OER catalytic property [12], [13], [14], [15], [16]. These techniques include morphologies [17], creating ultrathin nanosheets [18], manufacturing heterostructures with controllable defects [19], adjusting constituent compositions [20] and adding foreign elements [20].

The sorption and transformation of reactive species with the lower energy barrier for oxygen evolution reaction are typically made easier by doping foreign elements into catalysts [21,22]. This method consistently modifies the electronic structures of the catalysts and introduces defects [23,24]. Electrocatalysts are mostly formed with transition metals (TMs), especially 3d TMs like Mn, Cr, Fe & Zn as dopants to normalize their chemical valances [25,26]. Typically, incorporating of Zn atoms into various transition metal oxides (TMO) would result in wide spread electrocatalytically active TMs vacancies to enhance OER activity [27], [28], [29], [30]. Recent research has shown that incorporating rare earth elements into TMs-based species, such as, by doping of samarium into host electrocatalysts or by creating heterostructures among active and dopant catalysts, significantly improves the electrochemical catalytic behavior of Sm_2O_3 electrocatalysts for the production of H_2 and O_2 [31], [32], [33], [34], [35]. Several researchers, such as Wei Gao et. studied the impact of rare earth TMs dopant on NiO host crystal lattice for OER activity. The electrochemical analysis demonstrates that the insertion of CeO_2 into embedded configuration has a significant impact rather than the loaded configuration. The CeO_2 doped materials exhibited the lowest Tafel slope and overpotential (η) value than the loaded configuration and pure NiO [36]. Bocheng Qiu et al. examine the effect of the CeO_2 dopant on interfacial sites of Co_3O_4. Their analysis shows that the insertion of dopant material on the octahedral site produced a small overpotential and Tafel slope of 265 mV and 68.1 mV dec^{-1}, respectively [37]. Zhengcui Wu et al. analyze the effect of Fe dopant material on NiO mesoporous nanosheet. The electrochemical analysis indicates that Fe doped NiO exhibited small overpotential of 206 mV @ 10 mA cm^{-2}, which might be related to small crystallite size producing a larger interfacial area that helps in adsorption of electrolyte ions [38].

All of these studies demonstrate the importance of introducing rare earth species into hosts and adding rare earth transition metal oxide to electrocatalyst surfaces to create heterogeneous structures, both of which show promise for modifying the electronic structure of interface-active zones and, in turn, increasing their electrocatalytic behavior. Therefore, it is yet unclear how surface-loaded Sm-based substances to form heterostructures or implanted Sm-based substances within host process (Scheme 1) will most effectively initiative the oxygen evolution reaction process. To provide useful recommendations for the design of enhanced electrocatalysts with an acceptable spatial layout for electrochemical process, a thorough understanding of all these factors is crucial.

The catalytic and structural variations in nickel oxide catalysts with diverse spatial arrangements of Sm_2O_3 inclusion and their related impacts on electrocatalytic activity are compared in this research work. The preparation and characterization of two rare earth transition metal-incorporated nickel oxide catalysts with distinctive configuration, namely the embedded configuration of Sm_2O_3 clusters/atoms doped nickel oxide (Sm-NiO-E) and the surface-loaded configuration of Sm_2O_3 nanoarray on nickel oxide (Sm-NiO-L), are carried out. Comparing the two catalysts, it is interesting to note that the Sm-NiO-E catalyst displays greater OER performance with a smaller η of 409 mV @ 10 mA cm^{-2}. The low-coordinated Sm_2O_3 groups in Sm-nickel oxide appear to be crucial in producing the greater electrocatalytically defects, enhancing the O_2 adsorption capability and facilitating the OER catalyst, according to X-ray photoelectron spectra and other spectroscopy and microscopy techniques. All of these comparisons make clear the benefits of combining Sm_2O_3 with NiO and go on to explain why doping clusters of Sm_2O_3 improved their catalytic capabilities, offering a fresh perspective on the various spatial configurations of Sm_2O_3 on NiO for improved OER catalysts.

Section snippets

Reagents

All of the reagents employed in the synthesis of spatial configuration are highly pure and purchased from Sigma Aldrich, such as nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), samarium nitrate hexahydrate ($Sm(NO_3)_3$. $6H_2O$), ammonium hydroxide (NH_4OH), oxalic acid ($H_2C_2O_4$. $2H_2O$) absolute ethanol (C_2H_5OH) were utilized without prior purification. The deionized water (DI H_2O, 18.5 Ωm.cm) was purchased from Merk Millipore.…

Fabrication of NiO

The sol-gel synthetic strategy was employed to fabricate the NiO, Sm-nickel…

XRD study

X-ray diffraction calculations were utilized to determine the crystallinity, purity and size of the fabricated materials. Fig. 1(a) illustrates the XRD diffractogram of all fabricated products with three distinctive peaks at 44.49°, 51.90° and 76.62° corresponding to indexed planes of (111), (200) and (220) well consistent with the PDF=00–004–0835 indicates the successful fabrication of NiO with the crystallite sizes of 32.11 nm exhibiting space group number and space group of 225 and Fm-3 m, …

Conclusion

In conclusion, two alternative spatial arrangement of the Sm-incorporated nickel oxide electrocatalysts are synthesized and examined to investigate the implications of these structural alterations on their OER activity as well as their crystallinity and electronic structure differences. The structural, morphological and chemical states of the doped fabricated materials were determined with various analytical techniques. The electrochemical tests suggest that the Sm-NiO-E display a low…

Compliance with ethical standards

Yes, this paper adheres to the journal's ethical guidelines.…

Research data policy and data availability statements

The data collected during research activity will be provided on reasonable request to corresponding author.…

CRediT authorship contribution statement

Salma Aman: Data curation, Writing – original draft. **Naseeb Ahmad:** Supervision. **Muhammad Bilal Tahir:** Data curation, Writing – original draft, Supervision. **Meznah M. Alanazi:** Writing – review & editing. **Shaimaa A.M. Abdelmohsen:** Writing – review & editing. **Rabia Yasmin Khosa:** Conceptualization, Methodology, Software. **Hafiz Muhammad Tahir Farid:** Data curation, Writing – original draft.…

Declaration of Competing Interest

This document contains no conflicts of interest in any way.…

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