

Highly Stable Oxygen Evolution Electrocatalysts Achieved by Surface Protection with a Permselective CeO_x Layer

Keisuke Obata,^a Kazuhiro Takanabe^{a,*}

^aKing Abdullah University of Science and Technology (KAUST), KAUST Catalysis Center (KCC) and Physical Sciences and Engineering Division (PSE), 4700 KAUST, Thuwal, 23955-6900, Saudi Arabia

*Corresponding author: kazuhiro.takanabe@kaust.edu.sa

Abstract: Transition metal oxide electrocatalysts for oxygen evolution reaction (OER) suffer from deactivation due to dissolution of materials. Herein, we report the stability of OER electrocatalysts can be improved by anodic deposition of CeO_x layer without changing the activity of catalysts underneath. Because CeO_x layer showed permselectivity which suppresses redox ions to diffuse through while it allows the OH⁻ to evolve O₂, we attribute the improved stability to its permselectivity preventing dissolution of catalysts. This approach can be applicable for NiFeO_x and CoO_x suggesting its universality and opening up a noble strategy to develop durable catalysts.

Keywords: water splitting, electrocatalysis, oxygen evolution.

1. Introduction

Highly active and durable OER electrocatalysts are required for sustainable H₂ production from water splitting reaction. Although many transition metal (hydr)oxides consisting of abundant elements, such as NiFeO_x, are active catalysts in alkaline solution, it is reported to degrade gradually during electrolysis associated with gradual dissolution of active sites.¹ For example, Speck et al. observed that the content of iron decreased after stability test at 200 mA cm⁻² for 24 h and they suggested that iron leached out as FeO₄²⁻.^{1a} Here, we present a noble approach to improve the OER stability by anodic deposition of a permselective CeO_x layer, uniformly coating on the electrocatalysts.²

2. Experimental

NiFeO_x was prepared on a Au coated fluorine doped tin oxide (FTO) substrate by cathodic deposition³ at -20 mA cm⁻² for 2 min in a solution containing 9 mM NiSO₄·7H₂O, 9mM FeSO₄·7H₂O, 50 mM NH₄OH and 25 mM H₂SO₄. CeO_x layer was deposited on NiFeO_x by applying constant anodic potential of 1.1 V vs. Ag/AgCl in a deposition solution containing 0.4 M Ce(NO₃)₃·6H₂O and 0.4 M CH₃COONH₄ for 6 h adapted from a previous report.⁴ pH of the deposition solution was adjusted to 7 by adding NaOH solution. All the depositions were performed under flow of Ar.

Electrochemical measurements were performed using a BioLogic VMP3 potentiostat. Hg/HgO (1 M KOH) and Ag/AgCl (Saturated KCl) were used as reference electrodes in alkaline and neutral solution, respectively. The potentials were reported with respect to the reversible hydrogen electrode (RHE). *R_u* was obtained by impedance spectroscopy and the reported potentials were *iR_u*-corrected. Amount of O₂ gas evolved from a gas tight electrochemical cell was quantified with a gas chromatograph equipped with a TCD detector (GC-8A; Shimadzu Co. Ltd).

3. Results and discussion

Cross-sectional SEM image shows that the CeO_x layer was formed on NiFeO_x uniformly with a thickness 100-200 nm (Fig. 1a). TEM image revealed that the layer contained nanoparticle aggregates and voids within the layer were observed (Fig. 1b). The overpotential of bare NiFeO_x

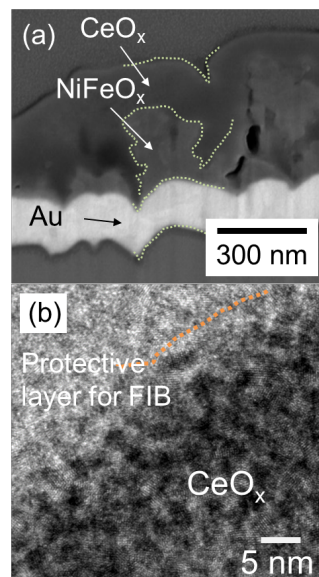


Figure 1. (a) cross-sectional SEM image of CeO_x/NiFeO_x. (b) High resolution TEM image of CeO_x layer.

increased by 60 mV during stability test in 1 M KOH at 20 mA cm⁻² for 96 h while that of CeO_x/NiFeO_x increased by ~10 mV suggesting that deposition of CeO_x layer successfully improved the stability of NiFeO_x catalyzt (Fig. 2a). Notably, when we compare the overpotential at the beginning of the stability test, there is no significant difference between bare and CeO_x/NiFeO_x, which indicates that the CeO_x layer did not perturb the activity towards OER. Tafel slope was also maintained ~40 mV dec⁻¹ after the deposition of CeO_x layer suggesting that reaction mechanism did not change by the presence of the CeO_x layer.

To investigate the nature of CeO_x layer in the electrolyte, Faradaic efficiency of O₂ was evaluated in the presence of reducing agents with the corresponding Stokes radii which were estimated from diffusion coefficients in aqueous solution⁵ (Fig. 2b). Clear improvement of selectivity was observed by the deposition of CeO_x in the presence of anions suggesting that charge plays a significant role for the diffusion through the layer rather than the size of molecules. Among the different alcohols, it showed better selectivity in the presence of bulkier alcohol, which implies that there is also a size exclusive effect. From these results, we attribute the improved stability of CeO_x/NiFeO_x to the permselectivity which prevents the diffusion of dissolved metal species to the electrolyte. The CeO_x layer also improved the stability of CoO_x in a neutral phosphate buffer solution suggesting its universality towards different OER catalyts.

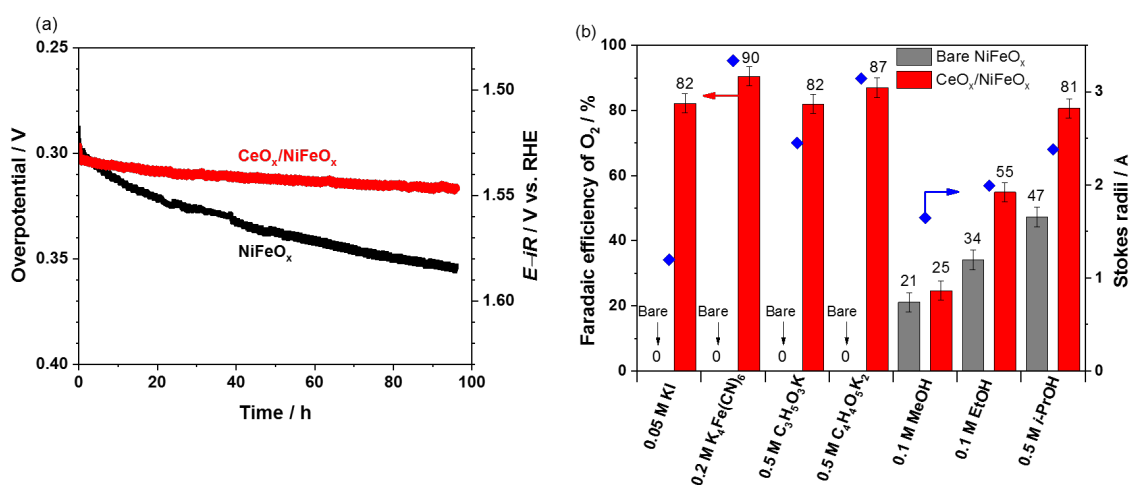


Figure 2. (a) Stability test by controlled current electrolysis at 20 mA cm⁻² in 1 M KOH. (b) Faradaic efficiency of O₂ during controlled current electrolysis at 10 mA cm⁻² in 1 M KOH in the presence of reducing agents with the corresponding Stokes radii.

4. Conclusions

Highly active and durable OER catalyts were developed by anodic deposition of CeO_x layer. The CeO_x layer demonstrated the permselectivity which regulates the diffusion of redox ions while it allows OH⁻ and O₂ diffuse through. The improved stability was attributed to the permselectivity which prevents the diffusion of dissolved metal species to the electrolyte. These results open up a new strategy to design durable OER electrocatalyts under harsh oxidative conditions.

References

1. a) F. D. Speck, K. E. Dettelbach, R. S. Sherbo, D. A. Salvatore, A. Huang, C. P. Berlinguette, *Chem.* 2 (2017) 590; b) M. B. Stevens, L. J. Enman, A. S. Batchellor, M. R. Cosby, A. E. Vise, C. D. M. Trang, S. W. Boettcher, *Chem. Mater.* 29 (2017) 120; c) M. Görlin, J. F. de Araújo, H. Schmies, D. Bernsmeier, S. Dresp, M. Gliech, Z. Jusys, P. Chernev, R. Kraehnert, H. Dau, P. Strasser, *J. Am. Chem. Soc.* 139 (2017) 2070.
2. K. Obata, K. Takanabe, *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.201712121.
3. C. C. L. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, *J. Am. Chem. Soc.* 135 (2013) 16977.
4. E. A. Kulp, S. J. Limmer, E. W. Bohannon, J. A. Switzer, *Solid State Ionics* 178 (2007) 749.
5. a) D. R. Lide, *Handbook of Chemistry and Physics*, 84th ed., CRC Press: Boca Raton, FL, (2003); b) L. Hao, D. G. Leaist, *J. Chem. Eng. Data* 41 **1996** 210.