Identifying active surface phases for metal oxide electrocatalysts: a study of manganese oxide bi-functional catalysts for oxygen reduction and water oxidation catalysis

Progress in the field of electrocatalysis is often hampered by the difficulty in identifying the active site on an electrode surface. Herein we combine theoretical analysis and electrochemical methods to identify the active surfaces in a manganese oxide bi-functional catalyst for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). First, we electrochemically characterize the nanostructured α-Mn2O3 and find that it undergoes oxidation in two potential regions: initially, between 0.5 V and 0.8 V, a potential region relevant to the ORR and, subsequently, between 0.8 V and 1.0 V, a potential region between the ORR and the OER relevant conditions. Next, we perform density function theory (DFT) calculations to understand the changes in the MnOx surface as a function of potential and to elucidate reaction mechanisms that lead to high activities observed in the experiments. Using DFT, we construct surface Pourbaix and free energy diagrams of three different MnOx surfaces and identify 1/2 ML HO* covered Mn2O3 and O* covered MnO2, as the active surfaces for the ORR and the OER, respectively. Additionally, we find that the ORR occurs through an associative mechanism and that its overpotential is highly dependent on the stabilization of intermediates through hydrogen bonds with water molecules. We also determine that OER occurs through direct recombination mechanism and that its major source of overpotential is the scaling relationship between HOO* and HO* surface intermediates. Using a previously developed Sabatier model we show that the theoretical predictions of catalytic activities match the experimentally determined onset potentials for the ORR and the OER, both qualitatively and quantitatively. Consequently, the combination of first-principles theoretical analysis and experimental methods offers an understanding of manganese oxide oxygen electrocatalysis at the atomic level, achieving fundamental insight that can potentially be used to design and develop improved electrocatalysts for the ORR and the OER and other important reactions of technological interest.

General information
State: Published
Organisations: Department of Physics, Center for Atomic-scale Materials Design, Theoretical Atomic-scale Physics, Stanford University
Contributors: Su, H., Gorlin, Y., Man, I. C., Vallejo, F. C., Nørskov, J. K., Jaramillo, T. F., Rossmeisl, J.
Pages: 14010-14022
Publication date: 2012
Peer-reviewed: Yes

Publication information
Journal: Physical Chemistry Chemical Physics
Volume: 14
Issue number: 40
ISSN (Print): 1463-9076
Ratings:
BFI (2018): BFI-level 2
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Scopus rating (2017): CiteScore 4.04 SJR 1.686 SNIP 1.089
Web of Science (2017): Impact factor 3.906
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 4.06 SJR 1.685 SNIP 1.113
Web of Science (2016): Impact factor 4.123
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): CiteScore 4.45 SJR 1.725 SNIP 1.205
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): CiteScore 4.29 SJR 1.771 SNIP 1.239
Web of Science (2014): Impact factor 4.493
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): CiteScore 4.05 SJR 1.72 SNIP 1.207
Web of Science (2013): Impact factor 4.198