Prediction of Oxygen Evolution Activity for NiCoFe Oxide Catalysts via Machine Learning

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ABSTRACT: Transition metal (such as Fe, Co, and Ni) oxides are excellent systems in the oxygen evolution reaction (OER) for the development of non-noble-metal-based catalysts. However, direct experimental evidence and the physical mechanism of a quantitative relationship between physical factors and oxygen evolution activity are still lacking, which makes it difficult to theoretically and accurately predict the oxygen evolution activity. In this work, a data-driven method for the prediction of overpotential (OP) for (Ni-Fe-Co)Oₓ catalysts is proposed via machine learning. The physical features that are more related to the OP for the OER have been constructed and analyzed. The random forest regression model works exceedingly well on OP prediction with a mean relative error of 1.20%. The features based on first ionization energies (FIEs) and outermost d-orbital electron numbers (DEs) are the principal factors and their variances (δFIE and δDE) exhibit a linearly decreasing correlation with OP, which gives direct guidance for an OP-oriented component design. This method provides novel and promising insights for the prediction of oxygen evolution activity and physical factor analysis in (Ni-Fe-Co)Oₓ catalysts.
machine-learning algorithm. The relationship between multiple physical features and OP properties was successfully determined, by considering valence electron number, relative atomic mass, atomic number, atomic radius (nonbonded), covalent radius, ionization energies (first), electron affinity, electronegativity (Pauling scale), and outermost d-orbital electron number. The random forest regression model works exceedingly well with a mean relative error of 1.20% evaluated on a hold-out set. The importance of physical features has been further analyzed. The first ionization energies (FIEs) and outermost d-orbital electron numbers (DE) are the principal factors, and their variances ($\delta_{\text{FIE}}$ and $\delta_{\text{DE}}$) exhibit a linearly decreasing correlation with OP. They give a direct guidance for an OP-oriented component design for (Ni-Fe-Co)O$_x$ catalysts. Our work aims to provide novel and promising physical insight for OER activity of (Ni-Fe-Co)O$_x$ catalysts.

All of the data used in this work were collected and screened from the published studies of Haber by a high-throughput experiment.\textsuperscript{27} We consider the oxide catalysts that belong to the Ni$_x$Co$_y$Fe$_z$ system, where the mole fractions of each element of $x$, $y$, and $z$ is constrained by $x + y + z = 100\%$. The data set consists of 496 entries (see the Supporting Information for details), covering the elemental composition in percent representing different (Ni-Fe-Co)O$_x$ materials and characterizing their overpotential (OPs) using a 10 s chronopotentiometry measurement at 10 mA/cm$^2$ in O$_2$-saturated 1.0 M NaOH(aq).\textsuperscript{27} The overall data set therefore possesses three features (input variables) represented by composition with respect to the elements and one target OP (output variable). Figure 1 gives the whole data visualization carried out with the Python programming language\textsuperscript{28} and the statistical data visualization library Seaborn.\textsuperscript{29} The composition for each of Ni, Co, and Fe ranges from 0 to 1 by even steps of 3.33 atom % and covers the whole composition space that may be formed. As the composition for each of Ni, Co, and Fe increases, the OP shows an overall trend of first decreasing and then increasing. This method can obviously show the optimal composition combination that minimizes the OPs of metal oxide catalysts. Complete and comprehensive data provide a reliable basis for a prediction model and physical fact analysis.

Physical features are critical for representing the intrinsic relationship between the latent fact and OP property. From the perspective of the atom level, nine accessible primary physical features by empirical experience given in Table 1 are used, including the valence electron number, relative atomic mass, atomic number, nonbonded atomic radius, covalent radius, first ionization energy, electron affinity, Pauling scale electronegativity, and outermost d-orbital electron number. For Ni, Co, and Fe elements, their physical properties corresponding with these features are collected from The Royal Society of Chemistry’s interactive periodic table database.\textsuperscript{30} The composition ($C_i$) and the associated elemental properties were adopted to numerically represent each catalyst sample with the featured transformation functions of eqs 1 and 2 for the purpose of converting the original chemical element space to a primary physical features space. For each catalyst sample in the 496 entries, $X$ calculates the weighted average of the element content corresponding to each physical feature, and $\delta_X$ produces the variance for each physical feature reflecting the physical difference of chemical element. In eqs 1 and 2, $C_i$ is the mole fraction of each element and $P_i$ corresponds to the properties of each element, respectively. Thus, 18 descriptive features that may be physically relevant to the OP are constructed by $X$ and $\delta_X$. The original data set is transformed into a new data set with 496 × 18 shape (see the Supporting Information for details).

In order to remove the linear correlation between two variables, Pearson correlation coefficients were then calculated before machine learning. Pearson correlation coefficients can be described as

$$R_{ij} = \frac{C_i C_j}{\sqrt{C_i C_i C_j C_j}}$$

where $R$ is the correlation coefficient matrix, $C$ is the covariance matrix. Covariance indicates the level to which two variables vary together, and it belongs to [-1,1]. The closer the $\mid R_{ij}\mid$ value is to 1, the higher the linear correlation between the two variables is. The heatmap of Pearson correlation coefficients for the physical features and OP are shown in Figure 2. Features with an absolute value of correlation coefficient greater than 0.95 were considered highly correlated (the boxes in dark blue and dark red in Figure 2). In the highly correlated feature pairs, one can be linearly expressed and replaced by the other. For example, the correlation coefficient between $\text{VEN}$ and $\text{EA}$ is 1; thus, $\text{EA}$ is retained instead of $\text{VEN}$. Therefore, $\text{VEN}$, $\text{AN}$, $\text{EA}$, $\delta_{\text{VEN}}$, $\delta_{\text{RAM}}$, $\delta_{\text{AN}}$, $\delta_{\text{RA}}$, and $\delta_{\text{EA}}$ are excluded. Finally, the data set contains 496 entries with 10 features ($\text{RAM}$, $\text{RA}$, $\text{RC}$, $\text{FIE}$, $\text{EP}$, $\text{DE}$, $\delta_{\text{RC}}$, $\delta_{\text{FIE}}$, $\delta_{\text{EP}}$ and $\delta_{\text{DE}}$) and 1 target property.

The OP is plotted as a function of $\text{RAM}$, $\text{RA}$, $\text{RC}$, $\text{FIE}$, $\text{EP}$, $\text{DE}$, $\delta_{\text{RC}}$, $\delta_{\text{FIE}}$, $\delta_{\text{EP}}$ and $\delta_{\text{DE}}$, respectively, as shown in Figure 3. It is obvious that OP decreases first and then rises with the increase of FIE and DE. The optimal values of FIE and DE may be set at around 750 and 7 to achieve the lowest OP. As $\delta_{\text{RC}}$, $\delta_{\text{FIE}}$, $\delta_{\text{EP}}$, and $\delta_{\text{DE}}$ increase, OP decreases, and the phenomenon is more obvious for $\delta_{\text{FIE}}$ and $\delta_{\text{DE}}$.

Machine-learning algorithms can fit a data-driven overpotential model with the selected physical features as the input and the target property OP as the output. Before model
construction, model selection and parameter optimization ensure which algorithm together with the suitable parameters would perform the best and be considered. The data set with 10 features and 1 target property was split by 80% (397 data entries) as the training set and 20% (99 data entries) left as the testing set (hold-out set). Several well-known machine-learning algorithms were used, such as stochastic gradient descent regression (SGDR) with penalties of L1 and L2, lasso regression (Lasso), elastic net regression (ElasticNet), multi-layer proceptron (MLP), tree regression (TreeR), Adaboost regression (AdaBR), gradient boosting regression (GBR), random forest regression (RFR), logistic regression (LogisticR), kernel ridge regression (KernelRidge), Bayesian Ridge regression (BayesRidge), support vector regression (SVR) with radial basis function kernel, and k-nearest neighbor regression (KNR). Parameter tuning was performed by a grid search on the training set by 5-fold cross validation for each machine-learning model, and the parameter with the best average mean squared error was determined. Then, the model was trained with the best parameter on the training set. Figure 4 shows the mean squared errors (MSE) and the standard deviations for different models during model selection. GBR, RFR, KernelRidge and KNR models exhibit excellent MSEs and uncertainties, and among them RFR has the lowest MSE of 40.6.

Then, we retrained the RFR model with the optimized parameters on the training set and evaluated the metrics of MSE and mean relative error (MRE) on 20% testing set, respectively. Figure 5a shows the diagonal scatter plot for the predicted OP and the ground truth by the RFR model during training and testing on the basis of the transformed and selected data set. RFR performs the best with an MRE value of 1.20% and an MSE value of 49.79. Figure 5b shows the contour map of the predicted overpotential by the RFR model under different compositions. The RFR model performs well on the “unseen” hold-out data set, whose MSE value is only 9.19 higher than that in training process, illustrating that this

**Table 1. Material Physical Features, Abbreviations, Units and the Transformation Formulas**

| features                          | abbreviation | unit   | formula                                     |
|-----------------------------------|--------------|--------|---------------------------------------------|
| valence electron number           | VEN          |        |                                             |
| relative atomic mass              | RAM          |        |                                             |
| atomic number                     | AN           |        |                                             |
| atomic radius, nonbonded          | RA           | Å      | $X = \sum_{i=1}^{N} CP_i$                   |
| covalent radius                   | RC           | Å      | $\delta_X = \sum_{i=1}^{N} [P_i - \bar{X}]C_i$ |
| first ionization energy           | FIE          | kJ mol$^{-1}$ |                                           |
| electron affinity                 | EA           | kJ mol$^{-1}$ |                                           |
| electronegativity (Pauling scale) | EP           | -      |                                             |
| outermost d-orbital electron number | DE           | -      |                                             |

![Figure 2. Heat map of Pearson correlation coefficients for the physical features and OP.](image)

![Figure 3. OP as a function of RAM, RA, RC, FIE, EP, DE, δRC, δFIE, δEP, and δDE.](image)
model can be used for OP prediction with generalization capability in (Ni-Fe-Co)Ox catalysts.

Next the contributions each physical feature makes to the high-precision OP prediction model will be revealed. On the basis of the trained RFR model, the 10 physical features are ranked by their feature importance in Figure 5c. The greater contribution to high-precision OP prediction one feature makes, the higher the importance index is. δFIE and δDE are the most critical factors supported by the RFR model, and from the perspective of model precision, δFIE is more important than δDE. The importance indices of δDE and δFIE are relatively lower than that of δFIE and δDE but higher than the others. When the trends of the physical features (δFIE, δDE, DE and FIE) in Figures 3 and 5 are combined, the δFIE and δDE values can be used to give direct guidance to design an optimal component for Ni, Co, and Fe for excellent OP, by adjusting the contents of different elements to make the two simple factors δFIE and δDE greater.

In summary, a data-driven approach to predict the OP for (Ni-Fe-Co)Ox catalysts is proposed via machine learning. The physical features that are more related to the catalyst overpotential for the OER are constructed, covering valence electron number, relative atomic mass, atomic number, atomic radius (nonbonded), covalent radius, first ionization energy, electron affinity, electronegativity (Pauling scale), and outermost d-orbital electron number. The random forest regression model works exceedingly well with a mean relative error of 1.20%. The simple and easily accessed factors (δFIE and δDE) by the variances of first ionization energies (FIE) and outermost d-orbital electron number (DE) importance are captured, exhibiting a linearly decreasing correlation with OP. They give direct guidance for the OP-oriented component design for (Ni-Fe-Co)Ox catalysts. Our work aims to provide novel and promising physical insights into the OER activity of (Ni-Fe-Co)Ox catalysts.

Figure 4. Mean squared errors for different models during model selection.

Figure 5. Machine-learning model by RFR. (a) Diagonal scatter plot for the predicted OP and the ground truth by RFR. (b) Contour map of the predicted overpotential by the RFR model under different compositions. (c) Physical feature importance ranking by the RFR model.
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