Spinel Oxides as Catalysts in Alkaline Anion Exchange Membrane Fuel Cells for Sustainable Energy

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Abstract

Developing renewable energy technologies that meet human needs is essential for climate change mitigation, reducing air and water pollution, conserving natural resources, and enhancing energy security. We focus on electrocatalysts, specifically Spinel oxides in hydrogen fuel cells for sustainable energy conversion, where we evaluate electrochemical properties related to ions with varying charges or positions within the catalysts. One standout predictor of catalytic performance is the ionic Lewis acid strength of 2+ ions. Surprisingly, linear regression models using this descriptor perform well in cross-validation, nearly matching the performance of more complex linear and nonlinear methods with richer feature sets.

1 Introduction

The world's energy consumption heavily relies on fossil fuels, including coal, oil, and natural gas [1]. Additionally, refined products derived from fossil fuels, e.g., petroleum, serve as raw materials for a wide range of products such as fertilizers [2], plastics [3], medicines [4], textiles [5], and food additives [6]. With much of the world grappling with energy shortages, there has been a notable surge in the costs of oil, gas, and electricity, also resulting in record-high prices for consumer goods. In addition, the production and combustion of fossil fuels stand as the primary source of greenhouse gas emissions, including carbon dioxide and methane, which contribute to global warming [7].

In contrast, chemical fuels like hydrogen boasts three times the energy density of gasoline, and can be generated from renewable energy sources, such as the sun and wind, which naturally replenish on the human time scale [8], making it an ideal energy carrier. In this work, we center our attention on a specific type of hydrogen fuel cell known as alkaline anion exchange membrane fuel cells (AEMFCs) [8], a relatively recent technology receiving increasing interest over the past two decades. These fuel cells operate in alkaline media, enabling the use of non-precious-group-metal (non-PGM) electrocatalysts, which can potentially reduce costs by up to 40% compared to commercially available fuel cells with similar or even superior performance. However, the design of electrocatalysts remains a challenge in this field.

A commonly used crystal structure known as Spinel oxides follows a formula of AB_2O_4, where A and B represent metal cations having four or six coordination numbers, respectively, and O denotes oxygen anion. The available choices for cations are vast, with roughly 50 candidates for the A and B sites and the possibility of multiple cations coexisting in an AB_2O_4 structure, resulting in thousands of potential combinations. Various physical properties are important: ionic Lewis acid strength (iLas), electronegativity (en), ionization potential (ip), and ionic radius (r). Determining which properties predominantly influence catalyst behavior further complicates catalyst design efforts. Our analysis builds upon the work of scientists over the past decade, who have synthesized a limited number of Spinel oxides and evaluated their performance in oxygen reduction reactions (ORR) for hydrogen

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fuel cells. We aim to narrow down the feature set based on physical knowledge unravel the key factors governing catalyst behavior in AEMFCs.

2 Results and Discussion

We aim to create a simple interpretable machine learning model to help explain how the choice of cation influences a spinel oxide's performance as a catalyst. We compiled a dataset consisting of 59 Spinel oxide catalysts from studies in the past decade. A key metric for catalyst, half-wave potential [8], is used as our performance outcome of interest. To simplify the dataset, we calculated the average half-wave potentials for catalysts with the same composition, resulting in 38 data points. Chemical elements in the dataset I = {Mn, Fe, Co, Ni, Cu, Zn} can gain positive charges of 2 or 3, and form ions. Note that all elements in I can have 2 charges, whereas {Mn, Fe, Co} can only have 3-charge states. The site and charge were assigned based on the crystal field stabilization energy (CFSE) [9].

To describe ions, we rely on a set of key electrochemical properties P = {ilas, en, r, ip}. We made the assumption that ion properties are additive, allowing us to create linear models that describe an ion and its site (A or B) or oxidation states (2^+ or 3^+) with a collection of features. The value of feature $j \in \{1, \ldots, J\}$ for ion k is $w_{k,j}$. The presence of ion k in spinel oxide i is indicated by a binary variable $x_{i,k}$. We indicate the halfwave potential for spinel oxide i by y_i. A linear model with a set of features is then indicated by the assumption that

$$y_i = \beta_0 + \sum_{j=1}^{J} \beta_j \sum_k w_{k,j} x_{i,k}, \tag{1}$$

where the parameters $\beta_0, \ldots, \beta_J$ are fit via linear regression.

2.1 Linear regression results for electrochemical properties associated with site or ion charge

We fit two linear regression models to assess how well electrochemical properties predict half-wave potentials. We hypothesized that these properties alone might not provide a complete description, so we introduced interactions of these properties with other ion characteristics in two different models. In the first model, we interacted four electrochemical features {ilas, en, r, ip} with the ion's site occupation, examining whether the effect of each property varies depending on the ion's site within the crystal lattice, which can influence catalytic reactions. The second model interacted the same electrochemical features with the ion's charge, exploring whether the impact of each property differs based on the ion's charge. We expected this second model to offer greater interpretability, as electrochemical properties are inherently influenced by the ion's charge, as opposed to the site. Results from these two models are pictured below in Tables 1 and 2.

Table 1: Model incorporating features derived from combining ion properties by sites.

	coefficient	**standard error**	**t**	**P>|t|**
Intercept	1.63	2.90	0.56	0.58
A_ilas	-1.63	1.57	-1.03	0.31
B_ilas	-1.47	1.12	-1.31	0.20
A_en	0.94	0.58	1.64	0.11
B_en	-0.26	0.39	-0.68	0.50
A_r	0.56	0.54	1.03	0.31
B_r	-0.12	0.42	-0.31	0.76
A_ip	-0.01	0.01	-0.39	0.70
B_ip	0.003	0.01	0.26	0.80
R^2 = 0.64				

Although the R^2 values for these two models are comparable, the second model demonstrates slightly better performance, evident in its better $p-$value for the ilas_2 feature. This observation stands in contrast to previous studies involving other crystal structures, such as perovskites [10], where sites were considered a major influencing factor. It is worth noting that in Spinel structures, elements can occupy the A or B sites, or even both A and B sites [8], while in perovskites, elements (or ions) occupying different sites typically differ significantly in terms of species and size [10]. These

Table 2: Model incorporating features derived from combining ion properties by oxidation states (charge).

	coefficient	standard error	t	P>|t|
Intercept	-0.05	0.10	-0.47	0.64
ilas_2	-1.89	0.97	-1.95	0.06
ilas_3	-0.08	0.14	-0.55	0.59
en_2	0.55	0.55	0.99	0.33
en_3	0.05	0.20	0.26	0.80
r_2	0.26	0.39	0.66	0.51
r_3	-0.20	0.38	-0.54	0.60
ip_2	-0.005	0.01	-0.50	0.62
ip_3	0.003	0.004	0.91	0.37

R^2 = 0.60

results suggest that although the roles of different sites in crystal structures may appear important, the catalytic properties in the case of Spinel or perovskite structures may not be strongly dependent on the type of coordination but rather on the nature of the ions themselves.

2.2 Investigation of pairwise correlation between model features

Recognizing that upon inspecting the $p-$values, a substantial number of features do not appear to be statistically significant in the previously fitted models, and considering our chemical knowledge indicating that several electrochemical descriptors may be correlated, we hypothesized that these features exhibit collinearity. To explore this further, we computed pairwise correlations for the above two models as shown in Tables 3 and 4.

Table 3: Pairwise correlations between features by combining properties of ions based on A or B site they are occupying.

Features	**A_ilas**	**B_ilas**	**A_en**	**B_en**	**A_r**	**B_r**	**A_ip**	**B_ip**
A_ilas	1.00	-0.96	0.92	-0.92	-0.31	0.23	0.99	-0.96
B_ilas	-0.96	1.00	-0.97	0.94	0.44	-0.26	-0.97	0.99
A_en	0.92	-0.97	1.00	-0.95	-0.56	0.27	0.94	-0.97
B_en	-0.92	0.94	-0.95	1.00	0.42	-0.45	-0.93	0.96
A_r	-0.31	0.44	-0.56	0.42	1.00	-0.10	-0.35	0.43
B_r	0.23	-0.26	0.27	-0.45	-0.10	1.00	0.24	-0.32
A_ip	0.99	-0.97	0.94	-0.93	-0.35	0.24	1.00	-0.96
B_ip	-0.96	0.99	-0.97	0.96	0.43	-0.32	-0.96	1.00

Specifically, we observed correlations among three features {ilas, en, ip} for {A,B} sites. Surprisingly, in Table 3, these features also exhibit correlations across A and B sites. This finding suggests that although multicollinearity may not affect the accuracy of the model, combining ions based on their sites in Spinel structures does not reliably capture the effects of individual independent properties on the dependent feature in the model.

Table 4: Pairwise correlations of all features by combining properties of ions based on oxidation state.

Features	**ilas_2**	**ilas_3**	**en_2**	**en_3**	**r_2**	**r_3**	**ip_2**	**ip_3**
ilas_2	1.00	-0.58	-0.27	0.54	0.06	0.12	0.90	-0.52
ilas_3	-0.58	1.00	0.03	-0.89	0.24	-0.31	-0.62	0.93
en_2	-0.27	0.03	1.00	-0.02	-0.75	-0.02	-0.16	0.03
en_3	0.54	-0.89	-0.02	1.00	-0.22	-0.16	0.55	-0.66
r_2	0.06	0.24	-0.75	-0.22	1.00	-0.06	-0.05	0.22
r_3	0.12	-0.31	-0.02	-0.16	-0.06	1.00	0.20	-0.63
ip_2	0.90	-0.62	-0.16	0.55	-0.05	0.20	1.00	-0.58
ip_3	-0.52	0.93	0.03	-0.66	0.22	-0.63	-0.58	1.00

We also examined the pairwise correlations among all features in this model, as illustrated in Table 4. Generally, we observed that features show weaker correlations between 2+ and 3+ oxidation states compared to those based on A/B sites. This assessment suggests that the influence of oxidation states on catalytic performance may be easier to understand than the influence of the coordination of ions.

2.3 Single-feature models: development and validation of accuracy

Notably, the feature "ilas_2" stands out as the most influential one in the second model. We also trained a separate linear model using only "ilas_2", and it achieved a R^2-value of 0.56, indicating a roughly linear correlation with catalyst performance. Subsequently, we employed ten distinct regression methods from scikit-learn [11] to fit the preprocessed dataset with either eight features combined based on oxidation states or only the "ilas_2", as shown in Table 5. We utilized the leave-one-out cross-validation strategy, which involves iteratively training a model on all training samples except one and assessing its performance on the omitted sample.

Table 5: Comparison of performance of various regression models

Model		8 features		1 feature	
		MAE (Volt)	**std**	**MAE (Volt)**	**std**
Linear	OLS	0.051	0.043	0.049	0.039
	Ridge	0.050	0.042	0.048	0.039
	Lasso	0.050	0.042	0.048	0.039
	Elastic net	0.050	0.042	0.048	0.039
Nonlinear	RF	0.035	0.041	0.043	0.042
	KRR	0.042	0.044	0.042	0.044
	SVR	0.048	0.052	0.045	0.045
	GPR(kernel=DotProduct+WhiteKernel)	0.048	0.045	0.046	0.043
	GPR (kernel=RationalQuadratic)	0.042	0.043	0.043	0.042
	ANN (hidden_layer_sizes=2, activation='tanh')	0.046	0.043	0.057	0.052

MAE, mean absolute error; std, standard deviation; OLS, ordinary least-squares;
Ridge regression (\alpha=0.5); Lasso (\alpha=0.01 (8 features) or 0.0001 (1 feature));
Elastic net (\alpha=0.01 (8 features) or 0.0001 (1 feature));
KRR, kernel ridge regression (\alpha=0.05, kernel='rbf', \gamma=0.012);
SVR, supporting vector regression (kernel='rbf', C=2, \epsilon=0.001)
RF, random forest; GPR, Gaussian process regression;
ANN, artificial neural network using multi-layer Perceptron regressor.

We employed mean absolute error (MAE) as the evaluation metric, where lower MAE values indicate better performance. Surprisingly, linear regression using the single descriptor "ilas_2" is nearly as predictive in cross-validation as a range of linear and nonlinear supervised learning methods, despite the latter benefiting from a significantly richer feature set.

The initial results took us by surprise because, in our experimental evaluations, we typically placed emphasis on ions with higher oxidation states, specifically those with a 3+ charge [12]. However, upon closer examination, these results appear to be quite reasonable. During catalytic processes, there is a preference for binding energies to species (characterized by "ilas") to fall within a specific range—not too small and not too large [13]. This allows reactants to effectively bind to the catalyst while enabling products to readily detach from the catalyst surface, thereby preventing poisoning. One possible explanation is that metal cations tend to form strong bonds with reactants and products, making ions with lower binding energies more favorable.

An alternative explanation could be that our dataset only considered the initial states of ions within the catalysts before any experiments were conducted. In real operating conditions, it is common for the oxidation states of ions to undergo changes. These findings suggest that ions with a 2+ charge and low "ilas" values may have a greater propensity to alter their oxidation state. According to the model's predictions, ions like Mn2+, which exhibit low "ilas" values compared to other ions, have the potential to enhance the performance of fuel cells. This aligns with our prior knowledge, which

suggests that incorporating Mn as Mn2+ by adding Fe into the catalyst typically results in catalysts with exceptional performance.

3 Conclusion

We found that linear regression using a single descriptor, ionic Lewis acid strength for 2+ ions, provides a highly interpretable model for catalytic performance. However, the model selection and accuracy are constrained by the dataset's small size, a common challenge in energy science. In the future, we intend to enhance the models' robustness and predictive power by employing multi-task representation learning across multiple relevant datasets.

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