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Electrocatalysis: High-entropy alloys as a bridge between theory and experiment

Electrocatalysis plays a pivotal role in the energy transition. The efficiency of electrocatalytic conversion processes depends on the "activity" of the electrocatalyst. Equally important are its electrochemical stability as well as the abundance and affordability of the catalyst material. Achieving a combination of all these properties in a single catalyst material has been a persistent challenge. This material limitation has driven interest in exploring catalytic applications of alloys and more recently high-entropy alloys (HEAs) – materials composed of multiple elements in nearly equal proportions, as defined originally [1], [2]. First applied for optimizing mechanical properties in materials science [3], HEAs – or more general high-entropy materials (HEMs) – have now also emerged as a promising platform for discovering novel electrocatalysts with unique, tunable properties [4].

In the following, we discuss an approach that leverages their compositional complexity and the ability to "down-project" the material search to less complex compositions [5]. This approach demonstrates how HEMs offer an exciting opportunity to bridge the gap between theoretical predictions and experimental validation, accelerating the development of next-generation energy solutions. The description focuses on our own work as well as collaborative efforts and is not meant as a review but rather a personal perspective.

The most established method for comparing "Theory" and "Experiment" in electrocatalysis is the surface science approach [6]. Experimentalists work with electrocatalysts that have well-defined surface structures and compositions, such as single-crystal electrodes [7]. However, such experiments often require elaborate preparation of the catalysts and detailed characterization of their surfaces. In contrast, the predominant "Theory" approach employing density functional theory (DFT) calculations involves creating slabs of atoms with a defined structure and employing activity descriptors – such as the OH binding energy on this surface – to predict catalytic activity [8]. This theoretical approach has proven highly effective in describing known electrocatalysts and providing fundamental insights that enhance chemical intuition in the search for improved catalyst materials [9]. In selected cases, it has also shown predictive power in identifying better catalyst materials [10]. Nevertheless, this method predominantly focuses on relatively well-defined "model catalysts", whereas commercial catalysts are typically far more complex in structure and composition. A notable example from heterogeneous catalysis is ammonia synthesis, where the theoretical understanding substantially lagged behind its commercial application [11]. Additionally, comparisons between "Theory" and "Experiment" are often restricted to a limited number of materials. For instance, the Sabatier principle, which underpins volcano relationships in activity, is typically represented using a small dataset of measurements from different laboratories. Despite the possibility to normalize the data to the performance of benchmark materials, e.g., pure Pt [12], the logarithmic plots used in these analyses tend to obscure significant outliers from the general trend, which may result from limitations in the theoretical model or inconsistencies in experimental data across laboratories.

HEMs enable a substantial advancement of this strategy by combining the descriptor approach with machine learning techniques. In a recent work by Pedersen et al. [13] it has been shown that by combining Bayesian optimization with the descriptor approach in DFT calculations one can establish a correlation between the composition of a material and its catalytic performance towards the ORR. This "theoretical model" can be used to establish heat maps of the composition–activity relationship exhibiting areas of interest, which can be scrutinized further and constitute the prediction for the most active catalyst in the investigated composition space, see workflow in Figure 1.

Interestingly, the "theoretical models" exhibited a relatively smooth landscape, and hence a relatively small number of different compositions (< 100) was sufficient for the identification of the activity optima. Keeping in mind the large number of possible compositions if for example a grid with 5 at. % difference between the compositions is constructed, i.e., > 10 000, this was a surprising result. As a consequence, the "theoretical model" allows for an "experimental validation" either by high throughput screening of thin-film material libraries [14] as in the discussed case or by medium throughput screening of nanoparticle-based catalysts as demonstrated by Mints et al. [15]. The establishment of "theoretical models" for the composition–

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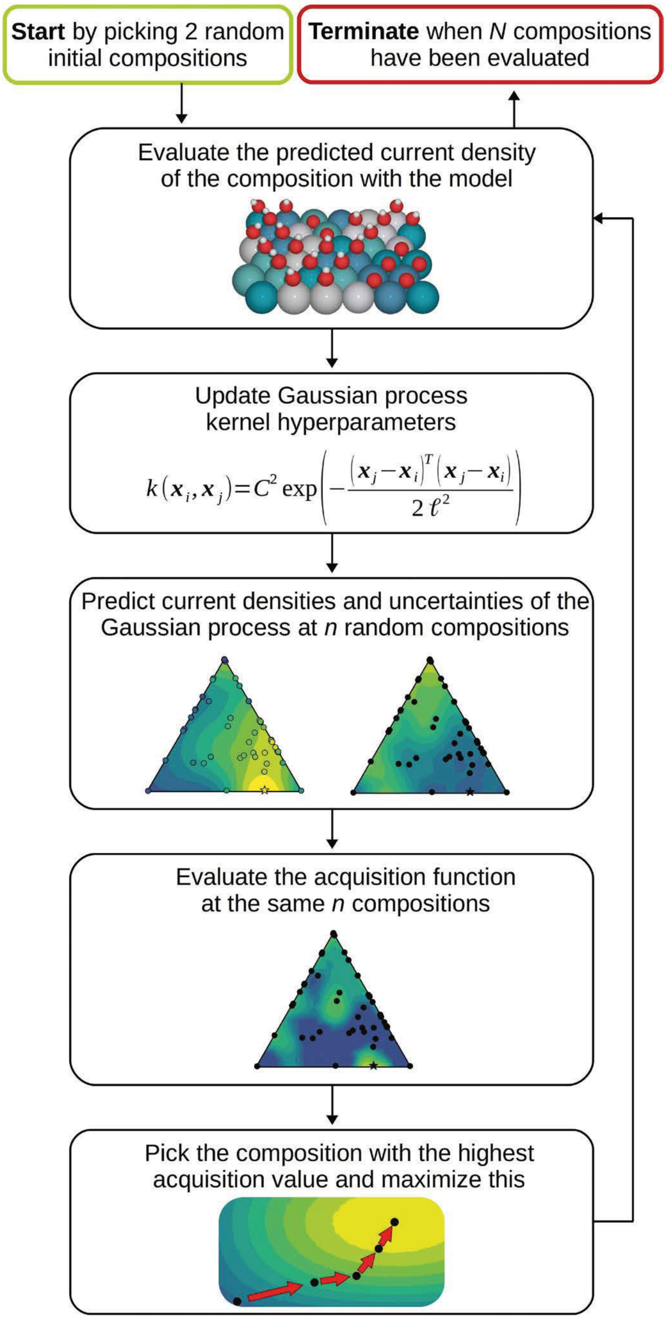


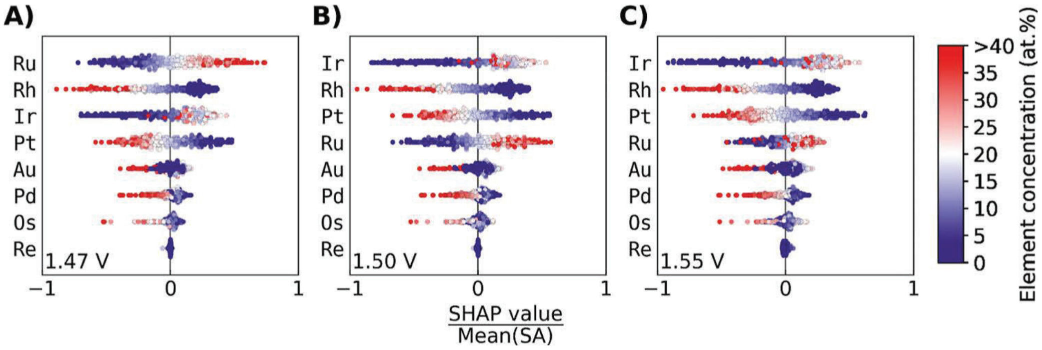
Fig. 1: Workflow of Bayesian Optimization scheme for the exploration of a composition space for identifying the most active electrocatalyst based on DFT calculations. Figure taken from reference [13]; Copyright by the authors CC BY-NC-ND 4.0.

activity relationship since then has been substantially accelerated by using extrapolations of the DFT calculations with the help of machine learning allowing the search for activity optima in higher dimensional (number of different metals) composition spaces [16]. For estimating DFT adsorption energies on HEA, surface machine learning algorithms are many orders of magnitude faster than DFT, which allows for studies that would have been impossible just a few years ago.

Also, the establishment of “experimental models” for the composition–activity relationship has seen significant advancements. It has been shown that with the help of Bayesian optimization, a loop consisting of catalyst synthesis – physical characterization – catalytic activity determination and the suggestion of new catalyst compositions to be synthesized and tested can be created [15]. The approach has been successfully applied for metallic electrocatalysts [15] as well as for oxides [17]. In the Bayesian optimization thereby one can weigh between the exploration of uncharted territories in the composition space and exploitation of compositions with expected high catalytic activity. Similar to the computational studies, relatively few (< 100) cycles were required for establishing optimal compositions. However, in the example by Mints et al. [15] we also realized that when focusing too much on exploitation “data clustering” occurs and it becomes difficult to observe trends or to construct an “experimental model” or to assess its predictive power, respectively. Hence a compromise between a full grid search and a search focused on exploitation needs to be found. Furthermore, procedures for establishing the quality of model establishing the composition–activity relationship becomes of prime interest. For this, cross validations such as leave one out cross validation (LOOCV) constitute a powerful tool. Also SHapely Additive exPlanations (SHAP) analyses have been proven useful to analyze the “importance” of the respective metal components in the HEM [15], [17]. For example, for HEM NPs containing Ru as well as Ir it could be observed that the “order of importance” changes from Ru at lower overpotentials to Ir at higher overpotentials, see Figure 2; a phenomenon that was interpreted as a consequence of the low electrochemical stability of RuO_x [17].

Despite a steep learning curve, there is plenty of room for advancing the experimental approach practiced in our group. For example, it needs to be carefully analyzed how to optimize the duration of the experiments to obtain enough data points in a reasonable time. Performing single optimization loops of cat-

Fig. 2: SHapely Additive exPlanations (SHAP) values for each of the elements in HEM nanoparticles exposed to acidic OER conditions at potentials of (a) 1.47, (b) 1.50, and (c) 1.55 V vs RHE. A positive SHAP value indicates a positive contribution to the OER current. Color of the points indicates the atomic percentage of the elements, as shown in the color bar on the right. Figure taken from reference [17]; Copyright by the authors CC-BY 4.0.



alyst synthesis – physical characterization – catalytic activity determination, i.e., synthesizing, characterizing, and measuring only one catalyst composition at a time before suggesting the next composition, is inefficient with respect to the time required to perform the experiments. Synthesizing a batch of several different compositions at a time is more efficient and Bayesian batch optimization should be pursued. Also the optimum number of experimental repeats of the same composition is currently unclear but when building an "experimental model" the identification of experimental outliers becomes very important. Several experimental considerations must be taken into account as performing several dozens of experimental optimization loops of high quality requires considerable time.

Despite the "infancy" of the presented approach to electrocatalysis, its impact and potential have already become apparent. This data-driven approach offers the opportunity of comparing "Theory" and "Experiment" based on multiple data points from a single experimental study. This is a crucial point as the descriptor approach is most powerful to describe trends in activity but not necessarily capable of delivering absolute activities or influences of the electrolyte used in the experiments. Nevertheless, the "Theory Model" is based on well-defined bulk and surface compositions and certain hypotheses, e.g., the activity descriptors. By comparison, the "Experimental Model" does not require any hypothesis and can be operated as a black-box model. Although it needs the composition of the catalyst as an input, it is important to note that the exact surface composition of electrocatalysts under operation conditions is extremely difficult, if not impossible, to determine; in particular in a medium- or high-throughput approach. However, the composition of the metal precursors in the synthesis and / or the bulk composition of the as prepared electrocatalyst can be determined with a reasonable effort. With the bulk compositions as input comparing "Theory Model" and "Experiment Model", it may become feasible to retrieve indirect insights on the "real surface" state of the electrocatalyst under operation conditions. This would be an extremely important information for catalysis. Known phenomena such as metal leaching upon contact to acidic conditions might be accessible in much more detail. Furthermore, by improving medium and high throughput structural characterization tools (in particular towards data analysis) additional factors such as structure, segregation effects etc. might be accessible in this approach in the future. Last but not least, we expect that the approach can be advanced to multi-objective optimization combining aspects of electrocatalyst activity, electrochemical stability, material abundance and price in an analysis of the best suitable material for a certain experimental condition.

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