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Machine Learning-Assisted Development of Platinum-Free RuNiCo Nanocages for Electrocatalytic Hydrogen Oxidation Reaction in Acidic Media

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ABSTRACT: Through data-driven synthesis involving 24 experiments from 16384 possible combinations (<1%), we developed two optimal electrocatalysts for the hydrogen oxidation reaction (HOR) in acidic media: PtIrRuNiCo nanowires and Pt-free RuNiCo nanocages. The objective function obtained in the Bayesian optimization (BO) process is highly correlated with the experimental current density for the HOR. The RuNiCo nanocages exhibited higher HOR activity than Ru because of the suppression of the surface oxide formation. Our BO-assisted approach accelerates the development of highly active electrocatalysts without requiring high-throughput synthesis.

KEYWORDS: *Hydrogen oxidation reaction, Electrocatalyst, Bayesian optimization, Platinum-free catalyst, Nanocage, Nanowire, Polymer electrolyte fuel cell.*

Polymer electrolyte fuel cells (PEFCs) generate electricity and heat from a renewable fuel of hydrogen and oxygen. In PEFCs, hydrogen oxidation reaction (HOR) and oxygen reduction reaction are catalyzed at the anode and cathode, respectively.¹ To catalyze the HOR in acidic media, Pt-based electrocatalysts are widely used because Pt shows high HOR activity with almost no energy loss.² Ironically, the high HOR activity of Pt directs our research interests from the development of Pt-free HOR electrocatalysts to Pt-free electrocatalysts for the oxygen reduction reaction.³⁻⁴ Thus, the development of Pt-free HOR electrocatalysts in acidic media remains challenging.⁵⁻⁹

Multimetallic alloy electrocatalysts including high-entropy alloy electrocatalysts, which contain five or more elements, possibly show higher catalytic activity and durability than single metallic electrocatalysts for the HOR in acidic media. The challenge of developing highly active and durable multi-metallic alloy electrocatalysts is the difficulty of optimizing the metal compositions in a vast compositional space over 10,000 possible compositions. For example, the number of the combination for synthesizing multi-metallic alloy electrocatalysts from seven metals with four synthetic conditions can be calculated to be $4^7 = 16384$. Identifying optimal configurations of multi-metallic alloys is a resource-intensive process.

AI-assisted catalyst development using Bayesian optimization (BO) enables the efficient navigation of the compositional landscape to pinpoint promising alloy compositions with enhanced electrocatalytic activity.¹⁰⁻¹² BO is a

global black-box optimization machine learning strategy of a computationally expensive objective function (OF). It iteratively finds new experimental conditions to optimize this OF with as few evaluations as possible.¹³ By pairing a surrogate model with an acquisition function, BO can systematically and efficiently explore a complex search space with relatively large number of potential candidates for discovering optimal electrocatalysts with unexpected compositions. For example, mesoporous ternary PtPdAu alloy electrocatalysts for the methanol oxidation were developed via BO by performing only 47 experiments out of 5151 possible compositions (less than 1%).¹⁰ Such an efficient approach can be coupled with high-throughput synthesis but also human-based synthetic approaches, enabling us to expand searching space for multi-metallic electrocatalysts.

The goal of this work is to develop Pt-free multimetallic electrocatalysts for the HOR in acidic media in a vast compositional space over 15,000 compositions ($4^7 = 16384$) using a machine learning-based optimization strategy. In this work, we developed two optimal electrocatalysts for the HOR in acidic media using BO: PtIrRuNiCo nanowires and Pt-free RuNiCo nanoparticles, which can convert to RuNiCo nanocages under electrochemical potential cycling.

Firstly, we optimized precursor compositions of Pt-containing electrocatalysts, taking into consideration maximizing the HOR electrocatalytic activity at 0.02 V vs. reversible hydrogen electrode (RHE) and minimizing Pt content at the same time. The catalysts were prepared from seven metal precursors of metal complexes with acetylacetonato ligands (**Table 1**), based on a modified synthetic procedure previously reported for PtNi nanowires (See

more details in Experimental section in the Supporting Information).¹⁴⁻¹⁶ All multimetallic catalysts were loaded onto a carbon support of Vulcan XC-72R and then electrochemical measurements of them were performed in a 0.1 M HClO₄ aqueous solution under H₂. The PtIrRuNiCo electrocatalyst was developed as the first optimal catalyst containing Pt. Next, the objective function (OF), which is a function of the current density at 0.02 V vs. RHE, was adjusted to apply a heavier penalty to Pt and Ir usage in the precursor composition, because Pt and Ir are much more expensive than Ru, which is the cheapest PGM.¹⁷ Finally, the Pt-free RuNiCo electrocatalyst was developed for the HOR as the second optimal catalyst.

Table 1. Summary of the amounts of metal precursors (in μmol) used for the synthesis of the catalysts and the current densities (j in mA cm^{-2}) at 0.02 V vs. RHE for the HOR in acidic media. The broken lines separate each BO step.

Step ^a	Entry No.	Pt ^b	Ni ^c	Ru ^d	Ir ^e	Co ^f	Cu ^g	Fe ^h	j ⁱ
0	1	50	25	25	$\frac{2}{5}$	0	25	0	0.42
	2	10	25	25	$\frac{2}{5}$	0	25	0	0.75
	3	50	25	0	$\frac{2}{5}$	25	25	0	1.96
	4	50	25	25	0	25	25	0	1.91
	5	25	0	25	0	25	25	25	1.13
	6	10	0	0	$\frac{2}{5}$	0	25	25	0.39
1	7	50	25	10	$\frac{2}{5}$	50	10	0	0.74
	8	25	25	50	10	25	0	0	1.42
	9	25	10	25	$\frac{2}{5}$	50	0	10	1.31
	10	25	50	25	0	25	0	0	1.40
2	11	25	25	25	0	10	0	0	1.18
	12	10	25	25	10	25	0	0	1.42
	13	50	25	0	0	25	50	0	1.33
	14	10	10	25	$\frac{2}{5}$	25	0	0	1.62
3	15	0	25	25	$\frac{2}{5}$	25	0	0	0.98
	16	10	10	50	$\frac{2}{5}$	25	0	10	1.26
	17	10	25	10	$\frac{2}{5}$	25	0	0	1.21

4	18	0	25	50	$\frac{2}{5}$	25	0	0	0.87
	19	10	10	25	$\frac{1}{0}$	25	0	0	1.13
	20	10	25	25	0	50	0	0	0.44
	21	10	25	25	0	0	0	0	1.36
	22	0	25	25	0	25	0	0	0.17
	23	0	50	25	0	0	0	0	0.04
	24	0	25	25	0	50	0	0	0.15

^a The datasets of the compositions and the j values from Nos. 1 to 6 were used as the initial training data (**Step 0**). The rest of the precursor compositions were suggested by the BO (**Steps 1–4**). In Steps 1–3, precursor compositions of the catalyst were optimized taking into consideration maximizing the j values and minimizing Pt content at the same time. In Step 4, the objective function for the BO was changed with a heavier penalty on Pt and Ir usage. ^b[Pt(acac)₂], ^c[Ni(acac)₂], ^d[Ru(acac)₃], ^e[Ir(acac)₃], ^f[Co(acac)₃], ^g[Cu(acac)₂], and ^h[Fe(acac)₃] were used as the precursors. ⁱ The j values were obtained from LSVs of the corresponding electrocatalyst at 0.02 V vs. RHE (iR corrected). LSVs were recorded at 10 mV s⁻¹ and 1600 rpm using a RDE in a 0.1 M HClO₄ aqueous solution under H₂.

We used a BO implementation named PHYSBO (Physics-based Bayesian Optimization)¹⁸ in Python programming language. PHYSBO is built based on the COMBO (COMmon Bayesian Optimization)¹⁹ library that focuses on accelerating data-driven materials discovery. Comparing to other BO implementations, PHYSBO is designed for materials science problems, making it more relevant to this study. Specifically, PHYSBO allows us to find better solutions for both single- and multi-objective optimization problems, automatically tune hyperparameters, and offer high scalability for high-dimensional optimization tasks, which are common in materials design and discovery (**Figure S1**). This high scalability is achieved using Thompson sampling for efficient selection of promising candidates, random feature map enabling rapid kernel approximations, one-rank Cholesky update to reduce computational overhead during model update, and MPI-based parallelization to reduce the calculation time for optimizing the acquisition function. PHYSBO package was successfully used in several materials optimization problems.²⁰⁻²² **Figure 1** illustrates how BO is used in an active learning scheme to find the optimal catalyst. This design searches for a catalyst with maximum current density and minimum ratios of expensive metals of Pt and Ir at the same time.

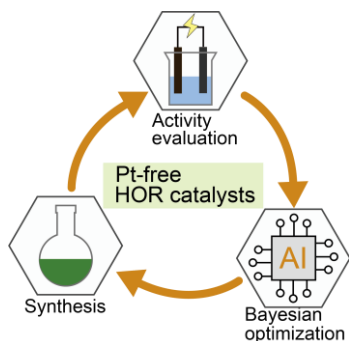


Figure 1. Schematic representation of BO-assisted development of Pt-free electrocatalysts for the HOR in acidic media. In this work, six datasets were used as the initial training data and then the BO cycle was repeated four times. The optimal Pt-free RuNiCo catalyst was developed by 24 experiments from $4^7 = 16384$ possible combinations from seven elements (Pt, Ni, Ru, Ir, Co, Cu, and Fe) and four initial precursor amounts (0, 10, 25, and 50 μmol).

We designed the OF that penalizes higher amounts of Pt in the final BO round. The penalty was applied on the content of Pt and Ir as in eq. 1:

$$OF = \text{current density@0.02 V vs. RHE} / \text{penalty} \quad (1)$$

where the *penalty* is a coefficient that increases with the increase of the sum of Pt_{ratio} (and Ir_{ratio} in the final round). This coefficient was tuned using the available training data. PHYSBO maximizes this function. A total of 24 catalysts were prepared out of $4^7 = 16384$ possible combinations from seven elements (Pt, Ni, Ru, Ir, Co, Cu, and Fe) and four initial precursor amounts (0, 10, 25, and 50 μmol) though BO (**Figure 1**). Initially, six catalysts (Entry Nos. 1-6 in Step 0 in **Table 1**) were prepared for BO training. Linear sweep voltammograms (LSVs) of their catalysts supported on the carbon black with an ionomer of Nafion were recorded using a rotating disk electrode (RDE) in a 0.1 M HClO_4 aqueous solution under H_2 . The precursor amounts used for the synthesis of multimetallic catalysts were optimized based on their HOR current density in mA cm^{-2} at 0.02 V vs. RHE (**Table 1** and **Figures S2-S25**) though the data-driven synthesis. The loop of the synthesis, the electrochemical measurement, and the prediction of the set of precursor amounts by BO was repeated (**Figure 1**). In each cycle, BO provides four catalyst candidates for synthesis and characterization. Notably, a plot of the OF against the experimental data of the current density gives a high correlation (**Figure 2** and **Table S1**). It visualizes how the Pt amount in the reaction precursor affects the OF. This plot indicates that the HOR activity trend highly depends on the Pt precursor amount. Finally, we obtained the promising candidates of the PtIrRuNiCo catalyst (No. 14) as the Pt-containing catalyst and the RuNiCo catalyst (No. 22) as the Pt-free HOR catalyst (**Table 1**). Further analysis of these two catalysts was mainly performed.

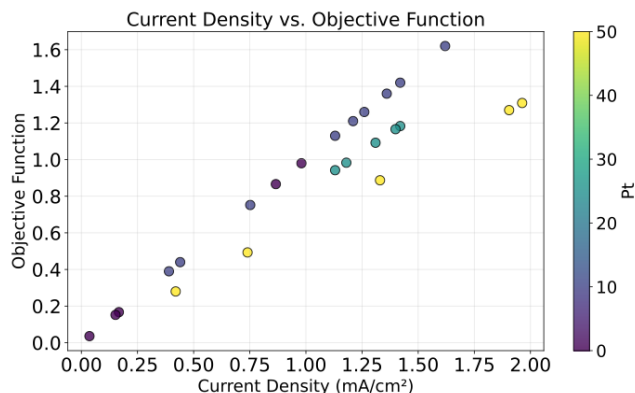


Figure 2. A plot of the OF, which is a function of the current density at 0.02 V vs. RHE, against the current densities of the catalysts prepared in this work. This confirms that OF is highly correlated with the experimental current density for the HOR. The color bar indicates the Pt amount (μmol) used in the reaction precursors. This illustrates PtIrRuNiCo catalyst (No. 14) with high current density (1.62 mA cm^{-2}) and low Pt amount (10 μmol), and the optimal Pt-free RuNiCo catalyst (No. 22) with current density (0.17 mA cm^{-2}). The values of the OF are summarized in **Table S1**.

The PtIrRuNiCo/C electrocatalyst (No. 14) is the optimal catalyst with lowest Pt content in the precursors in this work. A LSV of PtIrRuNiCo/C is shown in **Figure 3**. The composition of the as-prepared PtIrRuNiCo electrocatalyst (No. 14) was determined to be Pt:Ir:Ru:Co = 30:25:44:1 by ICP-OES, where Ni was not detected. The mass activity (MA) of PtIrRuNiCo/C (No. 14) based on the PGM amount was determined to be $0.32 \text{ A (mg}_{\text{PGM}})^{-1}$ at 0.02 V vs. RHE for the HOR in a 0.1 M HClO_4 aqueous solution under H_2 . This value is higher than that of Pt/C ($0.11 \text{ A (mg}_{\text{PGM}})^{-1}$). The electrochemically active surface area (ECSA) of PtIrRuNiCo/C (No. 14) was determined to be $1.0 \times 10^2 \text{ m}^2 \text{ g}_{\text{PGM}}^{-1}$, based on CO stripping voltammograms (**Figure S26**). Note that PtIrRuNiCo/C is more tolerant to CO than Pt/C because more negative CO stripping potentials indicate lower CO chemisorption energies to the catalyst surface.²³⁻²⁴ Accelerated durability tests (ADTs) of 1,200 potential cycles from 0.1 to 1.15 V vs. RHE at 250 mV s^{-1} and 313 K in a 0.1 M HClO_4 aqueous solution under Ar showed that the 85% activity remains for the PtIrRuNiCo/C electrocatalyst (No. 14) (**Figure S27** and **Table S2**).

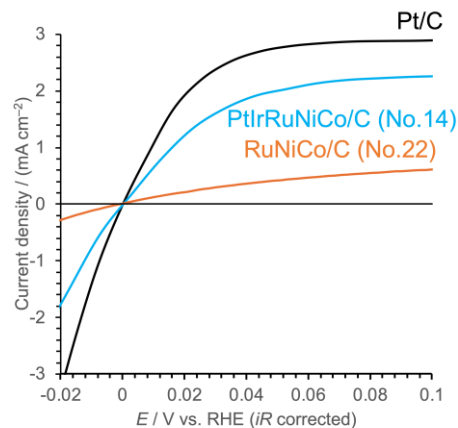


Figure 3. Representative LSVs of the two optimal carbon-supported catalysts, PtIrRuNiCo nanowires (No. 14) (in blue) and Pt-free RuNiCo nanoparticles (No. 22) (in orange), recorded at 1600 rpm and 10 mV s^{-1} in a 0.1 M HClO_4 aqueous solution under H_2 . A LSV of Pt/C (in black), which is commercially available carbon-supported Pt nanoparticles, is also shown as the standard HOR electrocatalyst for comparison.

Scanning transmission electron microscopy (STEM) images of PtIrRuNiCo/C (No. 14) show a nanowire morphology (**Figure S15**). The nanowire structure of the PtIrRuNiCo catalyst (No. 14) resembles those of PtNi nanowires previously prepared in the similar synthetic procedure.^{14–16} Pt-containing catalysts tend to form nanowires whereas nanoparticles were mainly found for Pt-free catalysts (**Figures S2–25**). It was reported that the formation of Pt nanoparticles follows the growth of nanowire morphology to obtain Pt alloy nanowires.^{25–26} In the current synthetic condition, the anisotropic growth process could be suppressed in the absence of Pt.²⁷

The RuNiCo catalyst (No. 22) was the optimal Pt-free electrocatalyst (**Table 1**). The as-prepared RuNiCo catalyst (No. 22) has a spherical morphology with an averaged 14 nm in diameter. Energy dispersive X-ray spectroscopy (EDS) mapping images of the as-prepared RuNiCo/C revealed that Ru mainly distributed on the surface of the nanoparticles whereas Ni and Co are distributed inside the nanoparticles (**Figure 4a**). The atomic composition of the as-prepared catalyst was Ru:Ni:Co = 22:67:11, determined by ICP-MS. X-ray absorption spectroscopy (XAS) of RuNiCo/C (No. 22) was performed at the Ru *K*-edge to understand the oxidation state of Ru in the catalyst (**Figure S28**). The edge position of RuNiCo/C can be found between those of the reference samples of Ru black and RuO_2 , indicating that Ru in RuNiCo/C is partially oxidized than the metallic state (**Figure S28**).²⁸ Since Ru is mainly placed on the surface of the nanoparticles (**Figure 4a**), the surface-exposed Ru is partially oxidized in RuNiCo/C.

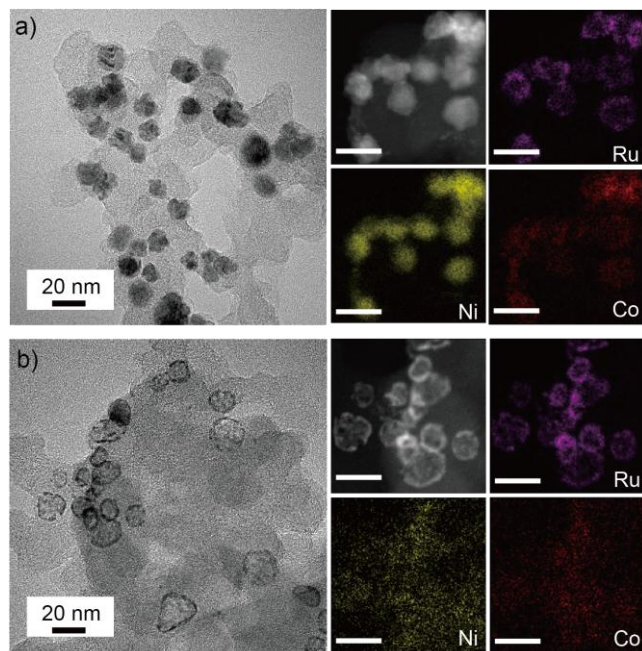


Figure 4. STEM, HAADF-STEM and EDS mapping images (purple: Ru; yellow: Ni; and red: Co) of the carbon-supported RuNiCo catalyst (No. 22) (a) before and (b) after the electrochemical cleaning process. The scale bars show 20 nm.

A nanocage structure was found for RuNiCo/C (No. 22) after the electrochemical cleaning in high-angle annular dark field (HAADF)-STEM and EDS mapping images (**Figure 4b**). The electrochemical cleaning process caused dealloying the core of RuNiCo nanoparticles with an overall mass loss of 28.5%, giving the RuNiCo nanocages. Thus, RuNiCo nanocages work as the active species for the HOR. The atomic composition of the RuNiCo nanocage was determined to be Ru:Ni:Co = 39:52:9 by ICP-MS. Based on this composition, the MA of the RuNiCo/C electrocatalyst was determined to be $0.012 \text{ A (mg}_{\text{PGM}})^{-1}$ at 0.02 V vs. RHE. This MA is approximately one order of magnitude lower than that of Pt/C. The ECSA of RuNiCo/C electrocatalyst based on CO stripping voltammograms was determined to be $82 \text{ m}^2 \text{ g}_{\text{PGM}}^{-1}$ (**Figure S26**). This ECSA value tends to be higher than those of Pt/C ($55\text{--}78 \text{ m}^2 \text{ g}_{\text{PGM}}^{-1}$).²⁹ This is possibly due to the nanocage structure. The HOR activity of RuNiCo/C remains about 22% after ADTs (**Figure S27** and **Table S2**).

The multimetallic alloy formation for RuNiCo/C (No. 22) suppresses the formation of ruthenium oxide than Ru/C, which is possibly associated with higher activity. LSVs of RuNiCo/C (No. 22) and Ru/C in the extended potential range up to 0.7 V vs. RHE under hydrogen are shown in **Figure S29**. Current densities for the HOR gradually decrease at $\geq 0.2 \text{ V}$ for RuNiCo/C whereas it happens more sharply at $\geq 0.1 \text{ V}$ vs. RHE for Ru/C. The decrease in current densities for the HOR is associated with the ruthenium oxide and/or hydroxide oxide formation at the catalyst surface.^{30–31} Because the potential for the oxide/hydroxide formation was shifted to more positive potentials for RuNiCo (No. 22), the ruthenium oxide/hydroxide formation is suppressed, which is possibly related to the multimetallic alloy formation.^{28,32–33} This result is in good agreement with the XAS results showing the reducing Ru valence state of RuNiCo/C, compared with RuO_2 (**Figure S28**).

In conclusions, we developed Pt-free electrocatalysts for the HOR via the machine learning-assisted synthesis using BO. PtIrRuNiCo nanowires (No. 14) show higher MA for the HOR in acidic media than Pt/C. Pt-free RuNiCo nanoparticles (No. 22) can be converted RuNiCo nanocages after electrochemical cleaning and then show higher HOR activity than Ru/C. This is possibly due to the suppression of ruthenium oxide/hydroxide formation at the surface of the RuNiCo alloy catalyst. The OF obtained in the BO process visualizes that the HOR activity highly depends on the Pt amount in the precursors. The MA of the RuNiCo nanocage is approximately one order of magnitude lower than that of Pt/C. Further improvement in catalytic activity is needed for Pt-free HOR electrocatalysts in acidic media.

The BO-assisted electrocatalyst development allowed us to find out the optimal synthetic condition of the RuNiCo catalyst by only 24 experiments out of 16384 combinations: in other words, only less than 1% of the possible conditions were tested to obtain the optimal catalyst. This work and other similar studies¹⁰ indicate that BO-assisted catalyst synthesis is efficient to develop highly active multi-metallic

electrocatalysts. We believe that BO-assisted synthetic approaches will accelerate the discovery of highly active and durable electrocatalysts even without using high throughput synthesis methods.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

STEM images and LSVs of each catalyst prepared in this work; Ru K-edge XAS data; LSVs before and after ADT; CO stripping voltammograms (PDF)

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Synopsis

