ACS APPLIED ENERGY MATERIALS

www.acsaem.org

Article

Microplate-Based Multielectrochemical Cells as a Platform for High-Throughput Parallel Experiments for Accelerating the Discovery of Multicomponent Electrocatalysts

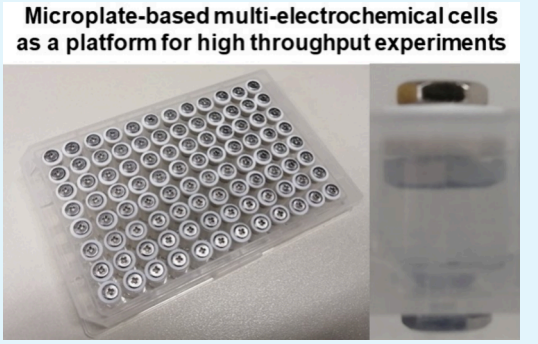
Shoichi Matsuda,* Ryo Tamura,* Misato Takahashi, Kazuha Nakamura, and Taiga Ozawa

Cite This: ACS Appl. Energy Mater. 2025, 8, 13714−13721

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The development of efficient electrocatalysts is a critical challenge in the advancement of energy conversion technologies. Among the diverse material candidates, multielement systems exhibit significant potential due to their compositional versatility. However, the vast number of possible combinations makes it infeasible to experimentally evaluate all candidates. High-throughput experimental approaches offer a promising solution. In this study, we developed a high-throughput platform combining parallel synthesis and evaluation based on a microplate-based electrochemical cell. The developed system enables the synthesis and electrochemical characterization of 96 samples in a parallel manner. To demonstrate its utility, we synthesized and evaluated 127 candidates for the oxygen evolution reaction (OER). Our results revealed that quaternary materials containing Fe, Ni, Cu, and Ag exhibit superior OER activity. Notably, removing any single element significantly decreased the activity, indicating the critical role of specific elements. Further analysis identified Ag and Ni as the key contributors to the enhanced OER performance. By further improvement of the synthesis throughput, this platform holds the potential to explore larger compositional spaces, accelerating the discovery of high-performance electrocatalyst materials.



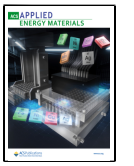
KEYWORDS: *high-throughput experiment, experimental automation, electrocatalyst, multicomponent materials, electrochemistry*

INTRODUCTION

There is an increasing demand for electrochemical energy conversion devices such as hydrogen fuel cells and hydrogen generation by water electrolysis. To improve the energy efficiency of such devices, decreasing the overpotential in the electrochemical reaction, such as the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), by introducing the proper electrocatalytic material is crucial. Noble-metal-based catalysts, such as Pt- and Ir-based materials, are utilized as electrocatalysts for these reactions. However, considering the widespread use of these energy conversion devices in accordance with the huge introduction of renewable energy, the development of non-noble-metal-based catalysts is demanded. For the development of efficient non-noble-metal-based electrocatalysts, a multielemental strategy is one effective approach for improving the catalytic activity of the material by suitably modulating the stability of intermediate species and/or cooperative effect between different elements.[1,2] However, there are a huge number of combinations of elements for designing multielement electrocatalytic materials, and it is not realistic to exhaustively search all of them. For example, if we consider 5 elements containing material and choose 5 from 20 candidates, the combination number is 20C5 = 15,504. Thus, a suitable experimental technique for accelerating the synthesis and evaluation of candidate materials is highly demanded for the development of multielement-based electrocatalysts. As a methodology for accelerating such multicomposition materials, high-throughput experiments are one of the promising candidates. The technology relating with high-throughput experiments for electrocatalysts has been intensively investigated in recent decades.[3,4] For the synthesis of electrocatalysts, the combinatorial synthetic procedure with the use of precursor solution, which is highly compatible with experimental automation, was one of the established methods. For example, Liu et al. reported automated high-throughput experiments for the synthesis of mixed metal oxide by using the inkjet printing method.[5] As a result, synthetic throughput over 1,000,000 samples/day has been demonstrated.

As described above, for the synthesis of electrocatalytic materials, several promising high-throughput experimental techniques have been developed. However, suitable high-

Received: July 4, 2025
Revised: August 31, 2025
Accepted: September 2, 2025
Published: September 9, 2025



https://doi.org/10.1021/acsaem.5c02030
ACS Appl. Energy Mater. 2025, 8, 13714−13721

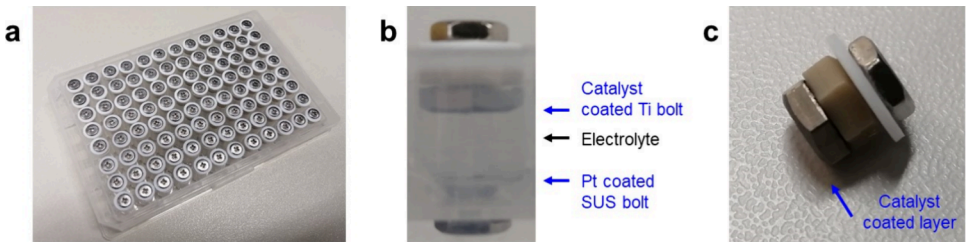


Figure 1. Photographic image of microplate-based electrochemical cells. (a) Overview of the whole part of the microplate-based electrochemical cell. (b) Cross-sectional view of each well. (c) Metal oxide thin film coated Ti-based bolt and Pt coated SUS-based bolt, which function as the working electrode and counter electrode, respectively.

throughput experiments for evaluating the electrocatalytic properties of these materials are not well established yet. Parallelization is one of the effective approaches for increasing the throughput of the measurement. Actually, even in the field of electrochemistry, there are several reports for the demonstration of parallel experiments for evaluation of electrocatalytic properties. For example, multielectrochemical cells capable of measuring 20 electrocatalysts at once have been reported.[6] However, in such a cell design, since the electrolyte and counter electrode are common for 20 working electrodes, there is concern for accuracy of the obtained data, such as the effect of the dissolution of metal ion species from the electrocatalyst. Thus, suitable high-throughput experimental technologies of electrochemical evaluation are not realized yet. Ideally, for realizing high-throughput search of multielement catalytic materials, all the procedures, including the synthesis, electrochemical measurements, and its integration, should be considered.

The use of a microplate as a multielectrochemical cell is an effective approach for realizing parallel experiments in electrochemical measurements in a high-throughput manner. For example, in the case of the 96-well type microplate, by using each well in the microplate as a miniaturized electrochemical cell by integrating electrodes and electrolyte, a 96-channel parallel electrochemical experiment can be realized. Microplates are widely used as a standard tool in high-throughput experiments within the field of bioscience with their specifications being standardized. As a result, a variety of compatible devices, such as liquid dispensing systems and robotic arm transport systems, are readily available. By leveraging these commercially available microplate-compatible devices, it becomes possible to construct automated and autonomous experimental systems in a cost-effective and efficient manner. Although the use of a microplate for electrochemical measurement in the field of biochemistry has been reported, the application of this technology in the field of electrocatalysts for energy storage devices has been limited. Recently, we constructed a microplate-based multielectrochemical cell for application in rechargeable lithium-ion batteries.[7,8] By fabricating 96 miniaturized battery cells in one microplate, containing the positive electrode, separator, electrolyte, and negative electrode, inside of each well, parallel experiments for battery performance evaluation were demonstrated. In addition, by integrating a suitable liquid handling unit and robotic arm, we constructed automated robotic experiments for high-throughput searching of multicomponent electrolytes. As a result, the system exhibited searching throughput over 1000 samples/day. In addition, by integrating machine learning techniques with the suitable orchestration software NIMO, the closed-loop autonomous experiments were also demonstrated.[9]

Based on these research backgrounds, in the present study, we developed a microplate-based electrochemical cell that is applicable for the exploration of an electrocatalyst. Notably, the developed microplate-based electrochemical cell has high compatibility with integration for high-throughput synthetic experiments of electrocatalysts. As a result, the developed system enables the synthesis and electrochemical characterization of 96 samples in a parallel manner. As proof of concept, we applied developed techniques for the investigation of multielement non-noble metal oxide based electrocatalysts for oxygen evolution in neutral pH conditions. As a result, the electrocatalyst composed of Fe, Ni, Cu, and Ag that exhibits superior OER performance via specific the synergetic effect of multielements was demonstrated.

EXPERIMENTAL SECTION

Synthesis of the Electrocatalyst. The metal oxide based thin film was synthesized by a thermal decomposition reaction. A titanium bolt with a head size of 6 mm diameter was utilized as the substrate. Manganese nitrate ($Mn(NO_3)_2{\cdot}6H_2O$, 98.0%, Wako), iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, 99.0%, Kanto Chemical), nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$, Kanto Chemical, 98.0%, Kanto Chemical), copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$, 99.0%, Kanto Chemical), scandium nitrate ($Sc(NO_3)_3{\cdot}4H_2O$, 99.0%, Junsei Chemical), zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99.0%, Wako), silver nitrate ($AgNO_3$, 99.8%, Wako), and ruthenium nitrate ($Ru(NO_3)_3$, 99.0%, Wako) were used as metal salts. A 50 mM nitrate metal salt dissolved ethanol solution was utilized as the precursor solution. For the drop-casting process, the liquid handling dispenser (Gyger, CERTUS) was utilized, and several kinds of precursor solution were injected on the surface of the Ti substrate. In our experiments, 96 Ti substrates were integrated into one module, and the solution drop-cast and precalcination processes were performed simultaneously. The equipment realized contactless dispensing of various kinds of liquid samples with different physical properties by utilizing eight individually controllable channels using microvalve technology and air pressure control. The metal nitrate containing precursor solution can be supplied to the dispenser from 100 mL sized bottles to the dispensing channel through the tube. Calibration was performed for each mother solution by adjusting microvalve and air pressure control conditions, which enabled the electrolyte injection with accuracy at the scale of 100 nL. Seven kinds of precursor solution were dispensed on the surface of the Ti substrate with appropriate solution volume ratio, and the solutions were mixed spontaneously. The solution drop-cast and precalcination (350 °C for 10 min) processes were repeated 10 times. In total, a 2.5 μmol/cm^2 amount of precursor was coated on the surface of the Ti substrate. Finally, the samples were calcined at 450 °C in 1 h.

Electrochemical Measurement. The solution of 0.1 M Na_2SO_4 dissolved water was utilized as an electrolyte solution. A Pt coated SUS bolt was utilized as counter electrode. Pt coating was performed by using a QUICK AUTO COATER (SC-701AT). Eight channels equipped with VMP3 (Biologic) were utilized for LSV measurement.

https://doi.org/10.1021/acsaem.5c02030
ACS Appl. Energy Mater. 2025, 8, 13714−13721

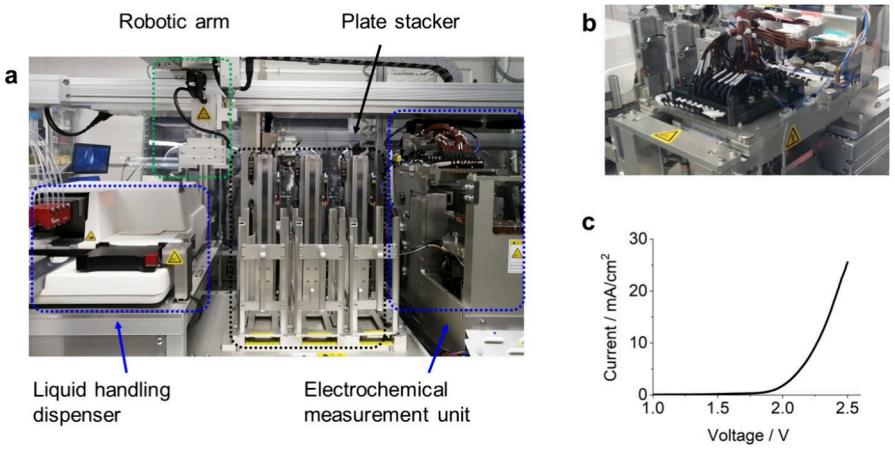


Figure 2. (a, b) Photographic image of the automated electrochemical measurement system. (a) Overview of the whole part of the system. (b) Magnified image of the electrochemical measurement unit. (c) LSV profile evaluating the OER performance of a RuO-based electrocatalyst.

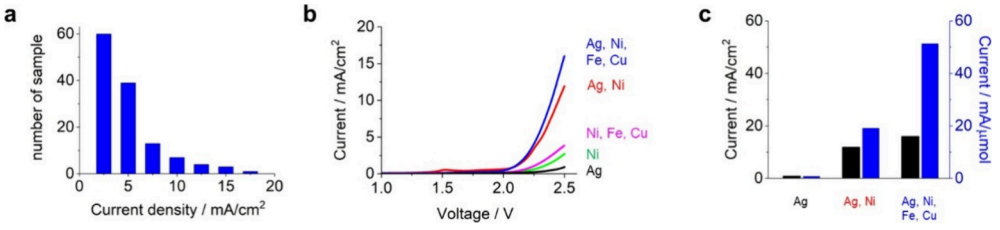


Figure 3. (a) Summary of the OER activity of the multielement metal oxide thin film. (b) LSV profile evaluating the OER performance of Ag-, AgNi-, and AgNiFeCu-based electrocatalysts. (c) Summary of the OER activity of Ag-based electrocatalysts.

The Keysight 34980A was adopted as the scanning system connected with the electrochemical measurement equipment. LSV measurement using three-electrode electrochemical cells was performed using Pt wire and Ag/AgCl as counter and reference electrode.

Characterization of the Multielement Electrocatalyst. X-ray diffraction (XRD; SmartLab, Rigaku), X-ray photoelectron spectroscopy (XPS; ULVAC-PHI, VersaProbe II), and TEM (JEM-ARM200F, JEOL) were used to characterize the multielement metal oxide thin film.

RESULTS AND DISCUSSIONS

We designed a microplate-based electrochemical cell that is suitable for the evaluation of the electrocatalytic activity of electrodes. The use of microplates as electrochemical cells offers many advantages in terms of improving the throughput of experiments, such as parallelization of measurements, continuous measurement by transporting cells with a robot arm, and preparation of electrolytes by using a liquid dispenser.

Table 1. Details of the Composition of the Top 10 Samples That Showed the Highest OER Activity

rank	category	Mn	Fe	Ni	Cu	Sc	Zn	Ag	mA/cm^2
1	7C4		○	○	○			○	16.04
2	7C2			○	○				14.96
3	7C5		○	○	○		○	○	14.49
4	7C3			○			○	○	14.31
5	7C2			○				○	11.94
6	7C5	○	○	○			○	○	11.06
7	7C4		○	○			○	○	10.81
8	7C5	○	○	○	○			○	10.63
9	7C3		○	○				○	9.48
10	7C4	○	○	○				○	9.32

Figure 1a shows the photographic image of microplate-based electrochemical cell that consisted of a polypropylene (PP)-based microplate, in which the metal oxide thin film coated Ti-based bolt and Pt coated SUS-based bolt are mounted on the top and bottom of the microplate and function as working and counter electrodes (Figure 1b). The Ti-based working electrode consists of four kinds of parts: SUS nut, PEEK nut, PTFE washer, and Ti bolt (Figure S1). Ninety-six independent wells are aligned in one PP-based microplate, and each well functions as an identical electrochemical reactor by introducing a suitable solution into each well as electrolyte.

For realizing the high-throughput experiment using the microplate-based electrochemical cell, an automated electrochemical measurement system was fabricated, which consists of (i) a plate stacking unit, (ii) a liquid handling dispenser unit, (iii) an electrochemical measurement unit, and (iv) a robotic arm (Figure 2a and Figure S2). The microplate-based electrochemical cells can be transferred between each unit by using the robotic arm. In the plate stacking unit, as many as 36 microplate-based electrochemical cells can be stored. The microplate-based electrochemical cells stored in the stacking unit move to the electrolyte injection unit by the robotic arm, and then the suitable electrolyte solution is injected into each well. After that, the microplate-based electrochemical cells move to the electrochemical measurement unit, and then suitable measurement is performed by using LSV or CV techniques. In this setup, electrochemical connections are established by bringing probes into contact with the Ti bolts at the top and SUS bolts at the bottom of the cell, applying appropriate pressure to ensure reliable contact (Figure 2b). Specifically, the system employs 96 probes connected to the top and another 96 probes connected to the bottom. These probes are, in turn, linked via cables to an electrochemical

https://doi.org/10.1021/acsaem.5c02030
ACS Appl. Energy Mater. 2025, 8, 13714−13721

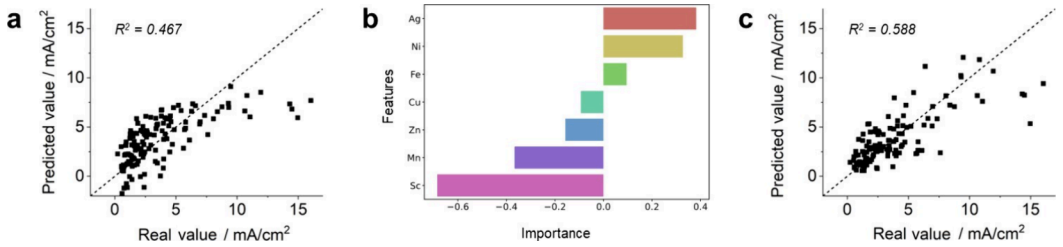


Figure 4. (a) Linear regression analysis with leave-one-out cross-validation. (b) Coefficients of the linear regression model for each elemental feature to the OER activity. (c) Random forest regression with nonlinearity

Table 2. OER Performance of the Samples That Contain Fe, Ni, Cu, or Ag

category	Ag	Ni	Fe	Cu	mA/cm^2
4C4	◯	◯	◯	◯	16.04
4C3	◯	◯	◯		9.48
4C3	◯	◯		◯	9.29
4C3	◯		◯	◯	7.45
4C3		◯	◯	◯	5.42
4C2	◯	◯			11.94
4C2	◯		◯		8.77
4C2	◯			◯	6.28
4C2		◯	◯		5.20
4C2		◯		◯	14.96
4C2			◯	◯	3.42
4C1	◯				0.91
4C1		◯			3.84
4C1			◯		2.94
4C1				◯	2.61

measurement device and a scanner, enabling precise and simultaneous electrochemical measurements across the system.

The electrochemical measurement system used in this study operates with eight channels. Each channel is connected to a scanning system that branches into 12 subchannels, enabling sequential measurements of 12 cells per channel. As a result, the system can perform parallel measurements of 8 cells in 12 loops. For each cell, linear sweep voltammetry (LSV) is conducted over a voltage range of 1−2.5 V at a scan rate of 5 mV/s. This requires 300 s per well. Therefore, the entire measurement of 96 wells on a single microplate can be completed within 90 min through 12 loops. The system is equipped with a stacker capable of holding up to 36 microplate-based electrochemical cells. By preloading microplates containing electrodes and electrolytes into the stacker, the system can complete the LSV measurement of one microplate in every 1.5 h. Once the electrochemical measurement of all the wells in one microplate is completed, the microplate-based electrochemical cells move back to the stacking unit. In this manner, electrochemical measurements are continuously performed. By integrating a series of equipment, the constructed system can perform continuous experiments for evaluation of the electrocatalytic property of electrodes. Such a high-throughput capability has huge potential to significantly accelerate the screening of electrocatalyst materials.

To demonstrate the high-throughput capability of the developed system for electrochemical measurements, we performed the LSV measurement for a total of 576 samples, which corresponds to six microplate-based electrochemical cells. All electrochemical cells consisted of an identical configuration, in which the Ti substrate was directly employed as the working electrode, and the Pt coated SUS-based bolt, which function as counter electrode, respectively. LSV was

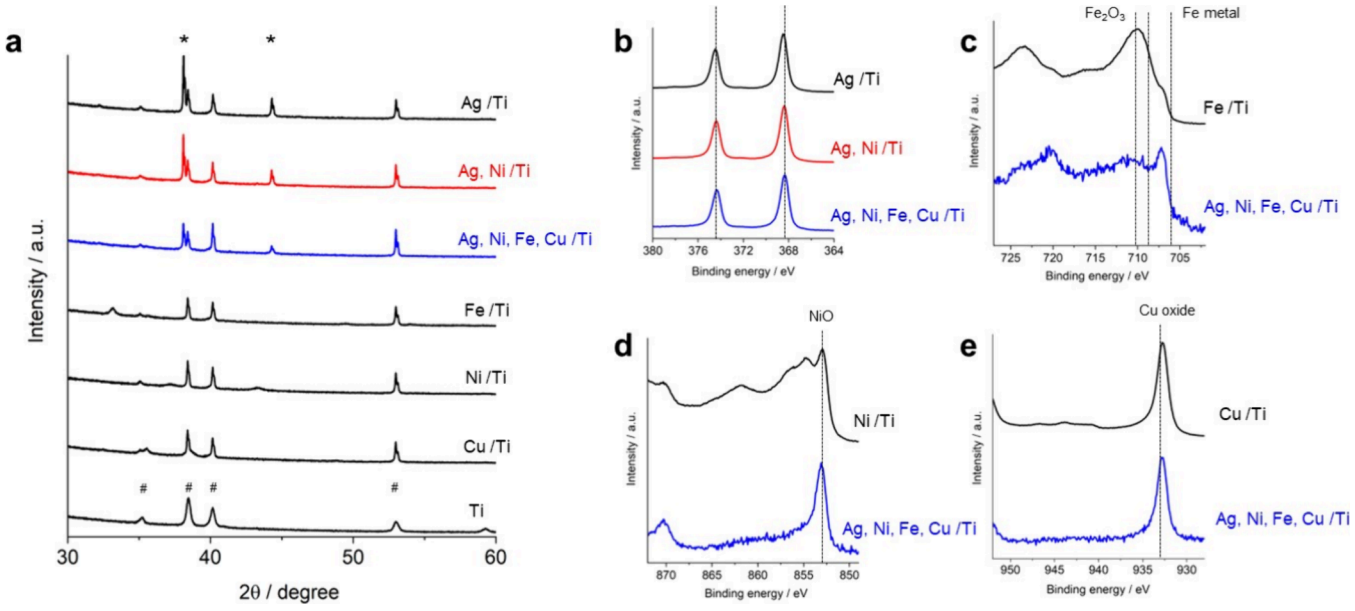


Figure 5. (a) XRD and (b−e) XPS profiles of Ag-, AgNi-, and AgNiFeCu-based electrocatalysts.

https://doi.org/10.1021/acsaem.5c02030
ACS Appl. Energy Mater. 2025, 8, 13714−13721

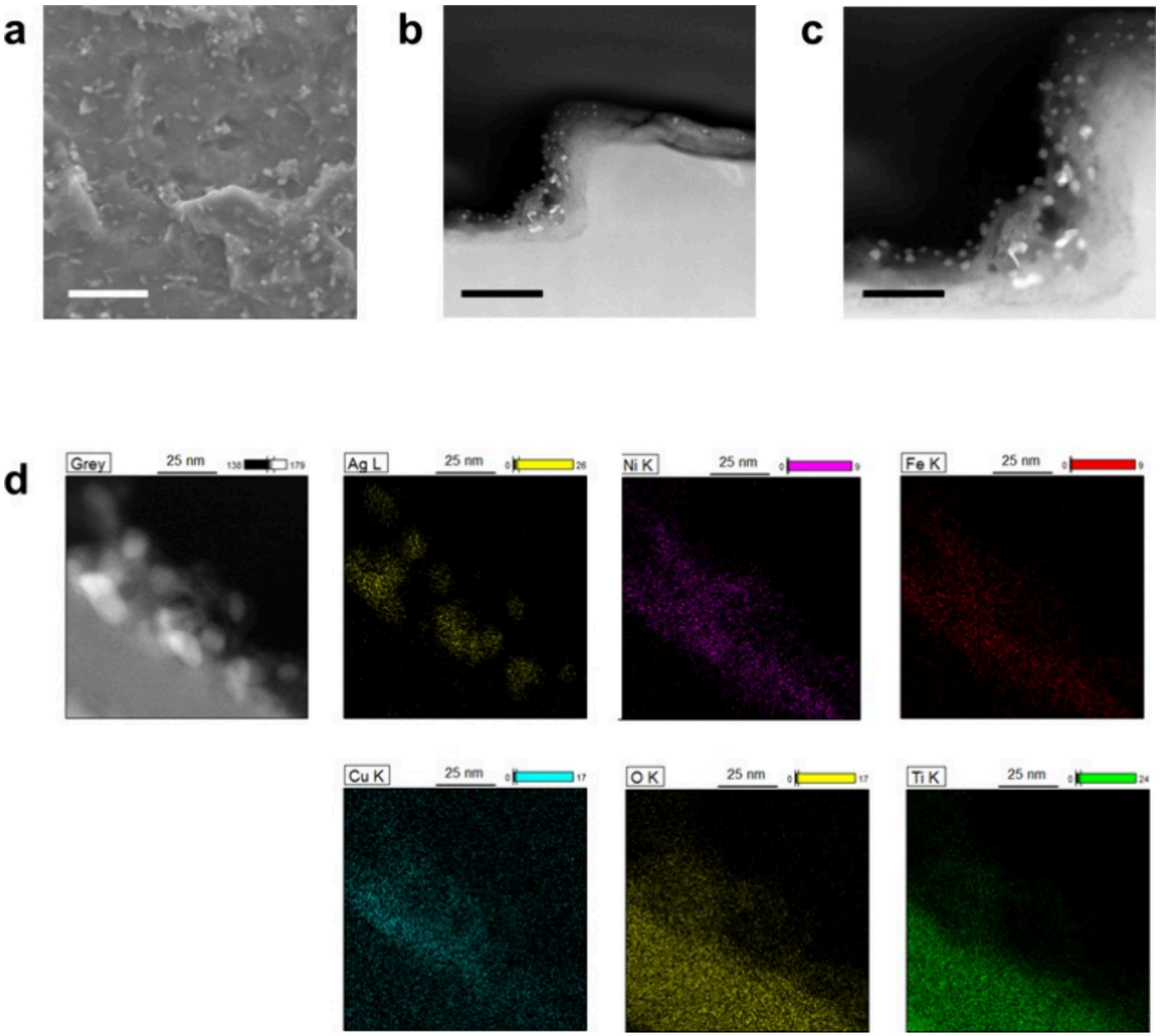


Figure 6. (a) SEM and (b–d) TEM images of the AgNiFeCu-based electrocatalyst. Scale bars are (a) 3 μm, (b) 200 nm, (c) 100 nm, and (d) 50 nm, respectively.

performed at a scan rate of 5 mV/s using an aqueous 0.1 M Na_2SO_4 solution as the electrolyte. Figure S3 presents representative LSV profiles obtained from three selected wells in the first microplate. The current density increased sharply with increasing voltage, revealing the progress of the OER. Similar LSV profiles were observed even in the sixth microplate, indicating consistent measurement performance across all wells. As result, an average current density of 1.8 mA/cm^2 at 2.5 V condition, with a standard deviation of 0.05 mA/cm^2, was obtained. These results demonstrate the high reproducibility of the developed system for continuous electrochemical measurements. Importantly, these experiments are completed within 10 h, revealing the superior throughput of this system.

To further evaluate the applicability of the system for more practical electrocatalytic measurements, we conducted LSV measurements using a RuO-based electrocatalyst, which is commonly used as an electrocatalyst for the OER. A distinct increase in current was observed around 1.8 V, corresponding to the onset of OER, and the current density reached 26 mA/cm^2 at 2.5 V. Even under such high current density conditions, stable LSV profiles were obtained, highlighting the suitability of the system for assessing the electrocatalytic activity of OER. Notably, no visible bubble formation was observed on the working electrodes during the LSV, suggesting that gas evolution did not significantly interfere with the measurements under these conditions. Here, it should be noted that during experiments involving substantial gas evolution, such as chronoamperometric measurements at elevated current densities, bubble accumulation on the electrode surface becomes increasingly problematic. This accumulation results in unstable current responses and poor reproducibility of the electrochemical measurement. Considering the critical influence of gas evolution on electrochemical performance, improvements in cell design are currently under consideration

https://doi.org/10.1021/acsaem.5c02030
ACS Appl. Energy Mater. 2025, 8, 13714−13721

within our research group and to be reported in the near future.

To demonstrate the novelty of the developed high-throughput parallel synthesis and evaluation system, we focused on the development of multielement metal oxides as electrocatalysts for the oxygen evolution reaction. The metal oxide based thin film formed on the surface of the Ti bolt was a suitable model material as a multielement electrocatalyst and was synthesized by the thermal decomposition process. As precursor solution, seven kinds of metal ion species—Mn, Fe, Ni, Cu, Sc, Zn, and Ag—were selected, and the multielement metal oxide thin film with the combination of 7Cn (n = 1 to 7) = 127 was systematically prepared. The liquid handling dispenser was utilized for drop-casting of precursor solution containing metal ions (Figure S4). The details of the synthetic procedure of the multielement metal oxide thin film are described in the Experimental Section. Although drop-casting of each precursor solution can be performed accurately and rapidly using a liquid handling dispenser, other processes such as drying, calcination, and sample transfer have not yet been automated and still require human intervention. As a result, the current experiment throughput of metal oxide thin film synthesis is limited to several batches per day, which correspond to approximately 200−300 samples per day. The integration of the whole process for realizing a fully automated system is now ongoing in our laboratory.

The OER activity of the prepared series of samples were evaluated by liner sweep voltammogram. The current value at 2.5 V is defined as the performance of the OER, and the results are summarized in Figure 3a. Although most of the samples exhibited a current value lower than 5 mA/cm^2, it can be seen that several samples showed OER performance higher than 10 mA/cm^2. The details of the composition of the top 10 samples that showed the highest OER activity among 127 samples are summarized in Table 1. Notably, in the top 10 samples, most of them consist of Ni and Ag, suggesting that these two elements play a crucial role in maximizing OER activity.

To identify the factors governing oxygen evolution reaction (OER) activity, we performed linear regression analysis on the data set comprising 127 samples. The analysis utilized the presence or absence of seven elemental components as features. The results by leave-one-out cross-validation are summarized in Figure 4a. In the low current density range (0−5 mA/cm^2), the model demonstrated a relatively high correlation with experimental OER currents. However, in the high current density range (≥5 mA/cm^2), the predictive accuracy was notably lower, indicating the need for more complex or additional descriptors to explain the OER behavior in this regime. Figure 4b illustrates the coefficients of the linear regression model for each elemental feature to the OER activity when all of the data are used as training data. Sc, Mn, Zn, and Cu showed negative contributions, whereas Ag, Ni, and Fe exhibited positive contributions. Among these, Ag and Ni were identified as the most influential elements, playing a critical role in maximizing OER activity. The results of coefficients revealed that the inclusion of Ag and Ni, along with the exclusion of Sc, is critical for achieving high OER activity. However, in regions with high OER activity, the linear regression model based solely on the presence or absence of elemental combinations failed to adequately explain the observed activity. This finding suggests the existence of complex interactions between elements that play a decisive role in determining OER activity. These interactions likely go beyond simple additive effects, emphasizing the need for advanced analytical approaches to capture the underlying synergistic effects among the elements. Note that using random forest regression with nonlinearity did not significantly improve the prediction of high OER activity (Figure 4c). Additionally, we confirmed that the contributions of each element in the random forest were similar to those in the linear regression model.

Next, we put our attention to clarifying the details of the multielement metal oxide electrocatalyst that showed the highest OER performance. The sample consisted of four kinds of metal ions: Fe, Ni, Cu, and Ag. In Table 2, the OER performance of the samples that contain Fe, Ni, Cu, or Ag is summarized. By comparing the results of samples of 4C4 and 4C3, it can be seen that eliminating one of the elements from the 4C4 sample results in lowering the OER activity. This result suggests a synergetic effect among the four elements. Figure 3b presents the LSV results for the OER evaluation of samples containing Ag and Ni. The results clearly show that the coexistence of Ag and Ni significantly enhances OER activity compared to samples with Ag or Ni alone. Furthermore, the OER activity is further improved in samples containing Ag, Ni, Fe, and Cu simultaneously, highlighting the synergistic effect of these elements. In particular, the sample consisting of Fe, Ni, and Cu showed a significant decrease of the OER activity (green curve in Figure 3b), suggesting that Ag is the key element for achieving high OER activity. Figure 3c summarizes the current density at 2.5 V and the OER activity per unit mass of Ag. Notably, the OER activity per unit mol of Ag in the AgNiFeCu sample is more than 10 times higher than that in the sample with Ag alone, demonstrating the substantial improvement achieved through multielement composition.

To confirm the results obtained by microplate-based electrochemical cells, we also performed the standard three-electrode-type electrochemical cells for selected samples. As results, we confirmed that the tendency of catalytic activity of OER observed in the microplate-based electrochemical cells was consistent with that observed in the standard three-electrochemical cell, suggesting the reliability of our setup (Figures S5 and S6).

We performed detailed characterization to reveal the physicochemical origin of the high OER activity. For this purpose, we selected three samples: Ag, AgNi, and AgNiFeCu. Figure 5a shows the XRD profile of the samples, revealing clear peaks assignable to metallic Ag. In contrast, for the other elements, no clear peaks are assignable to their metal or metal oxide compounds. As the amount of Ag increases, the peaks attributable to Ag become larger. The results of XPS in the Ag 3d region also support the formation of metallic Ag (Figure 5b). From the TEM analysis, the uniform distribution of 10−20 nm sized particles can be seen, which can be assigned to metallic Ag (Figure 6). In addition, the Fe, Ni, and Cu are distributed in the layer next to Ag nanoparticles. These results revealed that AgNiFeCu samples consist of metallic Ag nanoparticles distributed in the Fe, Ni, and Cu containing a metal oxide based matrix. In samples composed of Ag and AgNi, the majority of Ag particles are larger than 20 nm (Figure S7). In contrast, in AgNiFeCu samples, Ag particles are predominantly smaller than 20 nm. This observation suggests that the enhanced OER activity of AgNiFeCu is attributed to the reduced particle size of Ag, which leads to an increase in the effective specific surface area. The smaller particle size likely facilitates more efficient catalytic reactions,

https://doi.org/10.1021/acsaem.5c02030
ACS Appl. Energy Mater. 2025, 8, 13714−13721

thereby contributing to the observed improvement in OER performance.

The chemical states of Ni, Fe, and Cu were analyzed by using XPS (Figure 5c–e). For Ni, the single-element sample predominantly consisted of a mixture of $Ni(OH)_2$ and NiO, whereas the AgNiFeCu sample exhibited a NiO-rich composition. Similarly, Fe in the single-element sample was primarily in the form of Fe_2O_3, while it appeared as metallic Fe in the AgNiFeCu sample. These changes in the chemical states of Ni and Fe suggest that the electric state of Ag nanoparticles is modified by the interaction with the NiFeCu-based metal oxide matrix. This interaction likely plays a critical role in enhancing the catalytic performance of the material. On the other hand, Cu was present as Cu_2O in both the single-element sample and the AgNiFeCu sample, indicating no significant change in its chemical state. This suggests that Cu may contribute to suppressing the aggregation of Ag nanoparticles during the thermal decomposition process used to prepare the electrocatalyst. Further analysis of the electronic states of the material and the specific roles of each element in the synthesis process is currently ongoing in our laboratory.

CONCLUSIONS

In this study, we developed a microplate-based electrochemical cell (96-well format) and demonstrated its effectiveness in screening electrocatalyst materials. The developed system enables the synthesis and electrochemical characterization of 96 samples in one batch. The 96-well microplate-based electrochemical cell features wells that are physically isolated from each other, ensuring that electrochemical reactions in one well do not interfere with those in the other wells. This design enables the acquisition of highly reliable electrochemical data. By combining the system developed in this study with a suitable high-throughput electrode catalyst synthesis method, we successfully synthesized and screened multielement metal oxide electrocatalysts. As a result, we identified a catalyst composed of Fe, Ni, Cu, and Ag that demonstrated superior oxygen evolution reaction performance due to a specific synergistic effect among the multielements. This methodology provides a foundation for the development of a self-driving laboratory with the potential to significantly accelerate the discovery of novel electrode catalyst materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.5c02030.

Photographic image of the SUS nut, PEEK nut, PTFE washer, and Ti bolt; schematic illustration of the automated electrochemical measurement system.: LSV profiles obtained by the automated electrochemical measurement system; photographic image of the liquid handling dispenser; LSV profile evaluating the OER performance; summary of OER activity; and TEM images of samples (PDF)

AUTHOR INFORMATION

Corresponding Authors

Shoichi Matsuda − *Center for Green Research on Energy and Environmental Materials, National Institute for Material Science, Tsukuba, Ibaraki 305-0044, Japan;* orcid.org/0000-0002-0640-3404; Email: MATSUDA.Shoichi@nims.go.jp

Ryo Tamura − *Center for Basic Research on Materials, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan;* orcid.org/0000-0002-0349-358X; Email: TAMURA.Ryo@nims.go.jp

Authors

Misato Takahashi − *Center for Green Research on Energy and Environmental Materials, National Institute for Material Science, Tsukuba, Ibaraki 305-0044, Japan*

Kazuha Nakamura − *Center for Green Research on Energy and Environmental Materials, National Institute for Material Science, Tsukuba, Ibaraki 305-0044, Japan*

Taiga Ozawa − *Center for Green Research on Energy and Environmental Materials, National Institute for Material Science, Tsukuba, Ibaraki 305-0044, Japan*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsaem.5c02030

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The present work was partially supported by JST Mirai (Grant JPMJMI21EA), JST GteX (Grant JPMJGX23H2) and the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) Program: Data Creation and Utilization Type Materials Research and Development Project (Grant JPMXP1121467561). This work also received support from the National Institute for Materials Science (NIMS) Battery Research Platform. We are thankful to Dr. Ken Sakaushi and Dr. Watcharaporn Hoisang for fruitful discussions and technical suggestions.

REFERENCES

(1) Yao, Y.; Huang, Z.; Li, T.; Wang, H.; Liu, Y.; Stein, H. S.; Mao, Y.; Gao, J.; Jiao, M.; Dong, Q.; Dai, J.; Xie, P.; Xie, H.; Lacey, S. D.; Takeuchi, I.; Gregoire, J. M.; Jiang, R.; Wang, C.; Taylor, A. D.; Shahbazian-Yassar, R.; Hu, L. High-Throughput, Combinatorial Synthesis of Multimetallic Nanoclusters. *Proc. Natl. Acad. Sci. U. S. A.* **2020**, *117* (12), 6316–6322.

(2) Sakaushi, K.; Hoisang, W.; Tamura, R. Human-Machine Collaboration for Accelerated Discovery of Promising Oxygen Evolution Electrocatalysts with On-Demand Elements. *ACS Cent. Sci.* **2023**, *9* (12), 2216–2224.

(3) Gregoire, J. M.; Xiang, C.; Liu, X.; Marcin, M.; Jin, J. Scanning Droplet Cell for High Throughput Electrochemical and Photoelectrochemical Measurements. *Rev. Sci. Instrum.* **2013**, *84* (2), 24102.

(4) Jenewein, K. J.; Akkoc, G. D.; Kormányos, A.; Cherevko, S. Automated High-Throughput Activity and Stability Screening of Electrocatalysts. *Chem. Catal.* **2022**, *2* (10), 2778–2794.

(5) Liu, X.; Shen, Y.; Yang, R.; Zou, S.; Ji, X.; Shi, L.; Zhang, Y.; Liu, D.; Xiao, L.; Zheng, X.; Li, S.; Fan, J.; Stucky, G. D. Inkjet Printing Assisted Synthesis of Multicomponent Mesoporous Metal Oxides for Ultrafast Catalyst Exploration. *Nano Lett.* **2012**, *12* (11), 5733–5739.

(6) Hitt, J. L.; Li, Y. C.; Tao, S.; Yan, Z.; Gao, Y.; Billinge, S. J. L.; Mallouk, T. E. A High Throughput Optical Method for Studying Compositional Effects in Electrocatalysts for CO2 Reduction. *Nat. Commun.* **2021**, *12* (1), 1114.

(7) Matsuda, S.; Nishioka, K.; Nakanishi, S. High-Throughput Combinatorial Screening of Multi-Component Electrolyte Additives to Improve the Performance of Li Metal Secondary Batteries. *Sci. Rep.* **2019**, *9* (1), 6211.

(8) Matsuda, S.; Lambard, G.; Sodeyama, K. Data-Driven Automated Robotic Experiments Accelerate Discovery of Multi-Component Electrolyte for Rechargeable Li−O2 Batteries. *Cell Reports Phys. Sci.* **2022**, *3* (4), No. 100832.
(9) Tamura, R.; Tsuda, K.; Matsuda, S. NIMS-OS: An Automation Software to Implement a Closed Loop between Artificial Intelligence and Robotic Experiments in Materials Science. *Sci. Technol. Adv. Mater. Methods* **2023**, *3* (1), No. 2232297.

https://doi.org/10.1021/acsaem.5c02030
ACS Appl. Energy Mater. 2025, 8, 13714−13721