Supporting Information

Automatic Robot System for Machine Learning–Assisted High-Throughput Screening of Composite Electrocatalysts

Masanori Kodera* and Kazuhiro Sayama*

Global Zero Emission Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba West, 16-1, Onogawa, Tsukuba, Ibaraki, 305-8569, Japan

Table of Contents

Experimental Procedures

Sample preparation

Co, Mn, Fe, and Ni solutions (0.02 M) were prepared using cobalt (II) 2-ethyl hexanoate (65 wt% in mineral spirits (12 wt% Co); Strem Chemicals, Inc.), manganese (II) 2-ethyl hexanoate (40 wt% in mineral spirits (6 wt% Mn), Thermo Scientific), iron (III) tris(2-ethyl hexanoate) (mineral spirit solution (6 wt% Fe); Fujifilm Wako Chemicals), and nickel (II) 2-ethyl hexanoate (toluene solution (6 wt% Ni); Fujifilm Wako Chemicals), respectively. Butyl acetate was used as the solvent.

The mixed solutions (10 µL) were deposited on separate fluorine-doped tin oxide (FTO)-coated glass plates (Sigma-Aldrich; 5 mm × 30 mm) and dried at 348 K on a hot plate. The dried samples were calcined at 773 K for 30 min in an electric furnace, naturally cooled to room temperature, and picked up by the pick-up arm for electrochemical measurements.

Electrochemical measurements

Testing was performed in an H-type cell with a Nafion ion-exchange membrane using a typical three-electrode system (sample = working electrode, Ag|AgCl electrode = reference electrode, Pt wire = counter electrode).

Cyclic voltammograms were recorded at a scan rate of 50 mV s^{-1} in 0.5 M aqueous NaCl (pH ≈ 5.8; Fujifilm Wako Chemicals, 99%). Third-cycle current density at 2.0 V vs. Ag|AgCl was extracted as an explanatory variable for mapping and Bayesian optimization. The electrode area equaled 0.48 cm^2. The solution was gently stirred during measurements to maintain an effective electrode size.

Chronopotentiometric measurements were performed at a constant current of 1 mA for 200 s. Subsequently, a 20-µL aliquot of the electrolyte was transferred to a plate and mixed with 100 µL of 4 wt% N,N-diethyl-p-phenylenediamine sulfate in phosphate buffer (DPD; Kanto Reagents). The absorbance at 552 nm was recorded using a plate reader (Tecan, InfinitePro 200).[1] The faradaic efficiency (FE) of HClO formation (FE$_{HClO}$) was determined as

$$FE_{HClO} \text{ (\%)} = 0.1 \times n \times Abs \times V_{sol} \times F \times \varepsilon^{-1} \times Q^{-1} \times l_{sol}^{-1},$$

where n is the number of electrons required for HClO production ($n = 2$ in this case), Abs is the measured absorbance, V_{sol} is the solution volume (21 mL), F is the Faraday constant (96485 A s mol^{-1}), ε is the molar absorbance coefficient of the DPD reagent (21000 mol L^{-1} cm^{-1}), Q is the charge consumed during electrolysis (0.2 C), and l_{sol} is the light path length (0.68 cm). Considering that the equilibrium constant of Cl$_2$ + H$_2$O → HClO + HCl is 3.9 × 10^{-4}, a small amount of Cl$_2$ may be produced. Because, however, DPD reagent can detect both Cl$_2$ and HClO, we just denoted faradaic efficiency of HClO and Cl$_2$ as FE$_{HClO}$.

Stability tests were performed at a constant potential of 2.0 V vs. Ag|AgCl. The electrode stability was quantified as (current density after 1000 s)/(current density after 100 s).

Before electrochemical measurements, the solution is automatically replaced every time. First, the old solution inside the cell is pumped out using a pump, and then ion-exchanged water is introduced. Afterward, the ion-exchanged water is drained, and fresh solution is supplied into the cell.
In the case of 88 samples, the mixing solution step, the deposition step, the calcination step including cooling, the electrochemical measurements step took about two hours, two hours, three hours, and ten hours, respectively.

Bayesian optimization method

The code was written in Python3 using the Scikit learning library. Ten samples were randomly selected for maximization using a D-optimal design,[2,3] and Gaussian process regression (GPR) was then carried

out.[4–6] Expected improvement was used as an evaluation criterion.[7] Some compositions were prepared and tested more than once. In this case, the characteristic values were averaged before Bayesian optimization.
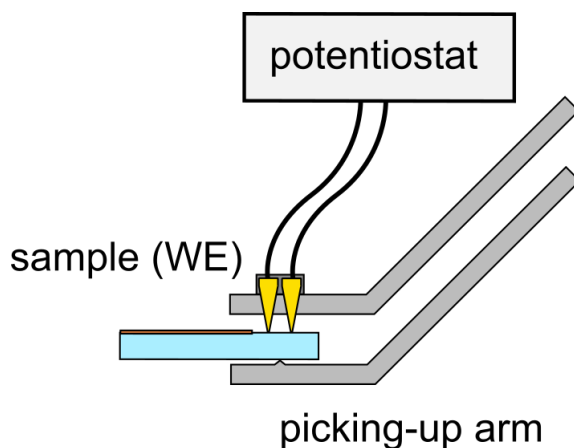
Figures

Figure S1. Schematic representation of the pick-up arm and electrocatalyst prepared on FTO. Prior to electrochemical measurements, the resistance between the two pins was measured by the resistance measuring instrument to ensure that the pick-up arm successfully grasped the sample. WE: working electrode.
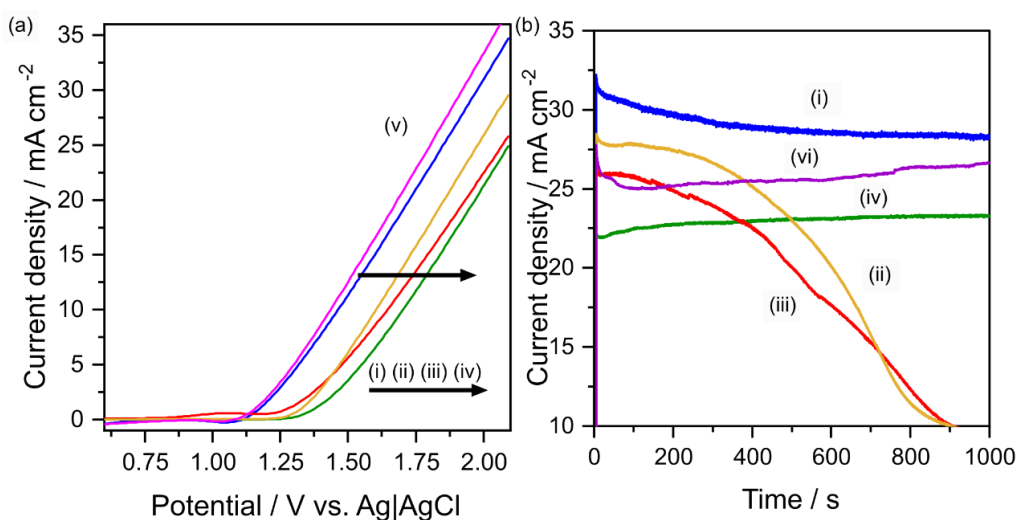

Figure S2. Typical (a) cyclic voltammograms and (b) current density as a function of time at 2.0 V vs. Ag|AgCl: (i) CoO_x/FTO, (ii) NiO_x/FTO, (iii) MnO_x/FTO, (iv) FeO_x/FTO, (v) $Co_{0.7}Fe_{0.2}Ni_{0.1}O_x$/FTO, and (vi) $Co_{0.2}Fe_{0.5}Ni_{0.3}O_x$/FTO. (v) and (vi) are the compositions exhibiting the highest current density and stability, respectively.

3

Dataset and Python code

The dataset which was used in this paper and a Python code is found at

https://github.com/masanorikodera/dd

The Python code was originally developed by Prof. Hiromasa Kaneko (https://github.com/hkaneko1985/python_doe_kspub) and modified by Masanori Kodera.

References

[1] L. Moberg, B. Karlberg, *Anal. Chim. Acta* **2000**, *407*, 127–133.

[2] M. Baroni, S. Clementi, G. Cruciani, N. Kettaneh‐Wold, S. Wold, *Quant. Struct. Relationships* **1993**, *12*, 225–231.

[3] S. Brandmaier, U. Sahlin, I. V Tetko, T. Öberg, *J. Chem. Inf. Model.* **2012**, *52*, 975–983.

[4] C. E. Rasmussen, H. M. De, *J. Mach. Learn. Res.* **2010**, *11*, 3011–3015.

[5] R. Iwama, H. Kaneko, *J. Adv. Manuf. Process.* **2021**, *3*, DOI 10.1002/amp2.10085.

[6] A. Seko, T. Maekawa, K. Tsuda, I. Tanaka, *Phys. Rev. B* **2014**, *89*, 54303.

[7] J. Snoek, H. Larochelle, R. P. Adams, *Adv. Neural Inf. Process. Syst.* **2012**, *25*.