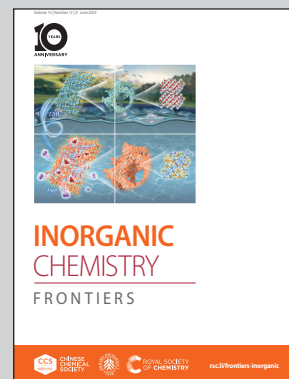


Showcasing research from Dr Tae Ho Shin's laboratory, Hydrogen Energy Material Centre, Korea Institute of Ceramic Engineering and Technology, Republic of Korea.

Enhancing CO₂ electrolysis performance with various metal additives (Co, Fe, Ni, and Ru) – decorating the La(Sr)Fe(Mn)O₃ cathode in solid oxide electrolysis cells

A promising metal-infiltrated ceramic electrode for high-temperature CO₂ electrolysis cells with a LaGaO₃-based solid oxide electrolyte is reported, suggesting accelerated chemical adsorption of CO₂ *via* metal additives on the ceramic electrode and presenting an insight into the surface activity of metal catalysts in CO₂ electrolysis.

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Cite this: *Inorg. Chem. Front.*, 2023, 10, 3536Enhancing CO₂ electrolysis performance with various metal additives (Co, Fe, Ni, and Ru) – decorating the La(Sr)Fe(Mn)O₃ cathode in solid oxide electrolysis cells†Sang Won Lee,^{†a,b} Tae Heon Nam,^{†a,c} Minkyu Kim,^a Seokhee Lee,^a Kyu Hyung Lee,^{†c} *^c Jong Hyeok Park^{†b} *^b and Tae Ho Shin^{†a} *^a

Perovskite oxide shows great promise as an alternative fuel electrode material in solid oxide electrolysis cells (SOEC) for the specific CO₂ electrochemical reduction, because of its excellent coking resistance. However, use of perovskite oxide is limited by its poor catalytic activity in CO₂ reduction. In this study, we investigated the use of various metal additives (Co, Fe, Ni, and Ru) on a La(Sr)Fe(Mn)O₃ (LSFM) fuel electrode for CO₂ reduction in a commercial infiltration process. Based on the electrochemical impedance spectroscopy (EIS) results, we determined the catalytic activity and reaction kinetics of CO₂ reduction for metal catalysts. In addition, the distribution of relaxation times analysis was conducted to investigate the adsorption and dissociation processes of CO₂ molecules for each catalyst. Consequently, when the Fe catalyst was applied in a LSFM fuel electrode for La_{0.8}Sr_{0.2}Ga_{0.8}Mn_{0.2}O₃ (LSGM) electrolyte-supported cells, an electrolysis performance of 2.201 A cm⁻² at 1.5 V in CO₂ electrolysis was obtained at 1123 K.

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Introduction

With the rapidly increasing energy demand worldwide, fossil fuel consumption, which accounts for 85% of the supplied energy, has caused energy and climate crises because of the associated CO₂ emissions. Due to sustainability challenges, global energy and emission policies aim for net-zero or net-negative emissions of greenhouse gases, including CO₂, by the year 2050.^{1–3} Therefore, researchers are currently focused on electrochemical CO₂ reductions of fuel and chemical feedstocks to create a sustainable society.^{4–7} However, the C=O bond energy in CO₂ shows an intrinsic stability of 806 kJ mol⁻¹, which makes CO₂ reduction challenging, especially at low temperatures.^{8–11} Moreover, solid oxide electrolysis cells (SOECs) show great potential as promising electrochemical devices for carbon capture and utilization, because they enable highly efficient direct conversion of CO₂ to CO. The operating

temperature of the SOEC (>1073 K) can accelerate the processes involved in CO₂ reduction, such as molecular adsorption and dissociation. In addition, CO, a product of CO₂ reduction, has been widely used in industrial applications, where it is smelted to metal by using reducing oxides or is converted to syngas by the Fischer–Tropsch process.^{12,13}

The electrochemical reactions in SOECs are mostly dominated by the fuel electrode, where the CO₂ reduction is performed at the electrode surface. The Ni-based fuel electrodes are commonly used in SOECs because of their high electrochemical activity and good conductivity for current collection. However, Ni electrodes suffer from inhibition of the redox instability, or deactivation of Ni due to a carbon buildup (coking) on the Ni electrode surface when directly exposed to a CO₂/CO atmosphere.^{14–16} Therefore, from the perspective of CO₂ electrolysis in SOECs, alternative materials with catalytic activity, electrical conductivity (EC), and durability in the CO/CO₂ redox reaction are essential. Consequently, perovskite oxide is attracting attention as a candidate because of its excellent CO₂ redox stability and carbon coking tolerance.^{15,17,18} Among these, the La(Sr)FeO₃-based perovskite oxides have high ionic and electrical conductivities, as well as catalytic properties because of the Fe⁴⁺/Fe³⁺ couple, which is compensated for by oxygen vacancies.¹⁹ The abundant oxygen vacancies in Fe-based perovskite oxides can provide active sites for CO₂ adsorption and dissociation.^{20,21} For example, Ishihara *et al.* have reported that Mn-doped La_{0.6}Sr_{0.4}Fe_{1-x}Mn_xO₃ used as a

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precursors was introduced into the porous LSFM electrode. After subsequent heat treatment, the metal catalysts formed on the surface of the LSFM electrode. The XRD analysis was performed to confirm the chemical stability and formation of the metal catalysts on the LSFM electrode after the infiltration process. Fig. 1 shows the XRD patterns of bare and metal-infiltrated LSFM after heat treatment at 1073 K for 1 h. The LSFM materials only showed a pattern corresponding to perovskite-based LaFeO_3 (JCPDS 37-1493), which has an orthorhombic structure as the dominant phase. After the infiltration process, the patterns confirmed the crystallinity of the perovskite phase without distinct impurity peaks of the secondary phases,

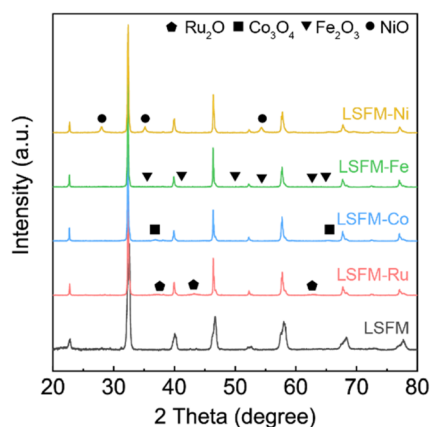


Fig. 1 X-ray diffraction (XRD) patterns of bare and infiltrated LSFM electrodes with various metal-based catalysts (Co, Fe, Ni, and Ru) after sintering at 1073 K.

which indicated the stability of the metal catalyst on the LSFM backbone. In addition, the metal-based catalysts were identified by their intrinsic peaks in the form of metal oxides. These metal catalysts were expected to improve cell performance by accelerating the adsorption and dissociation of the CO_2 molecules during the CO_2 electrolysis.^{25,26}

Fig. 2 shows the HR-SEM images which demonstrate the microstructure of the LSFM and the infiltrated LSFM electrodes. The images show that each metal particle is visible on the internal LSFM surface, leading to an increase in surface roughness. In addition, the EDS mapping indicates a high degree of overlap in the distribution of Co, Fe, Ni, and Ru, which is consistent with the LSFM backbone. These observations confirmed that the metal nanocatalyst is evenly dispersed across the LSFM surface. Although there are slight differences in particle size, the metal particles have high coverage and are well-distributed at the nanoscale, which can also be expected to have a nano size effect. These well-distributed nanoparticles are ideal for extending the reactive active sites to enhance the electrode reactions. In the electrochemical reactions, metal catalysts adsorb CO_2 molecules to form carbonate intermediates, which rapidly provide electrons to accelerate the dissociation reaction into CO and O^{2-} . In addition, the well-distributed nanoparticles are ideal for enhancing the electrode reaction by expanding the reactive active sites and triple-phase boundaries (TPBs).²⁷ Therefore, in addition to CO_2 electrolysis, the metal-infiltrated LSFM is superior to LSFM in humidified hydrogen fuel cells.

Fig. 3a shows the I - V curves of the cell containing the LSFM and infiltrated LSFM electrodes under humidified hydrogen at 1073 K. Overall, the addition of metal catalysts improved the

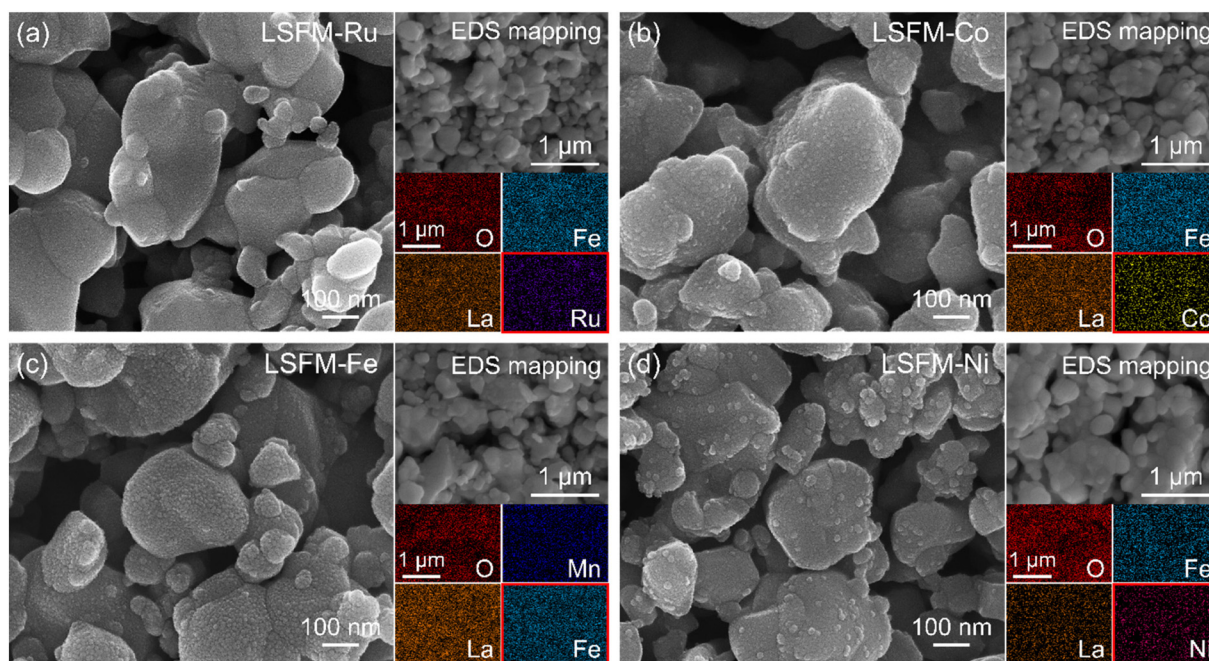


Fig. 2 Scanning electron microscopy (SEM) images and EDS mapping results taken for (a) LSFM-Ru, (b) LSFM-Co, (c) LSFM-Fe, and (d) LSFM-Ni electrodes after sintering at 1073 K.



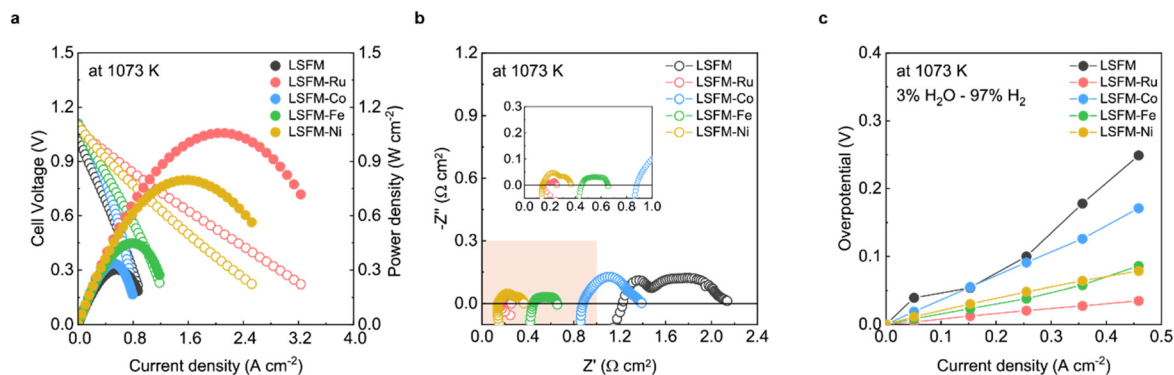


Fig. 3 (a) The I-V curves and (b) the impedance data of single cells of LSFM and infiltrated LSFM electrodes (Co, Fe, Ni, and Ru) at 1073 K under H₂O : H₂ (3%:97%). (c) The polarization overpotential is calculated from the impedance data.

performance of the cell. The LSFM-Ru electrode cell achieved the highest performance of approximately 1.05 W cm⁻² which is about twice the maximum power density of a bare LSFM cell (0.56 W cm⁻²). As shown in Fig. 3b, the ohmic resistance (R_o) was calculated from the intercept point of the high-frequency region along the real axis of the Nyquist-plots. After infiltration, the R_o decreases, which is likely to be because the metal precursor solution improves the interfacial stability between each particle and layer.²⁸ In terms of the polarization resistance, which accounts for the electrochemical reactions, the overpotential was estimated by using the current interruption method (Fig. 3c) as a function of current density. As expected, the electrochemical reaction of the bare LSFM was enhanced because of metal catalytic activity. For the LSFM-Ru, the overpotential was significantly decreased compared to that of the others at under humidified hydrogen (Ru > Fe ≥ Ni > Co). This result implies that the various metal catalysts decrease the molecular surface activation energy of the electrode, enhancing the electrochemical reaction of SOFC under a hydrogen atmosphere.

To evaluate the electrochemical performance of the CO₂ reduction for electrolysis, the cell containing the LSFM and

the infiltrated LSFM electrodes was tested under a blend of CO₂ : CO gases (50 : 50) at 1123 K, the results of which are shown in Fig. 4. Table 1 summarizes the open-circuit voltage (OCV), cell performance, and resistance values obtained from the EIS data with the different metal catalysts. In the CO₂ : CO (50 : 50) atmosphere, the OCV of the LSFM-based electrodes was approximately 0.96 V, which is close to the theoretical value expected from the Nernst equation, and this indicated the good gas-sealing of the cell.²⁹ Moreover, the satisfactory

Table 1 The electrochemical properties of CO₂ electrolysis with LSFM and metal-infiltrated LSFM at 1123 K: open-circuit voltage (OCV), the current density at 1.5 V, and the EIS results

Sample	OCV	Current density @1.5 V (A cm ⁻²)	R_o (Ω cm ²)	R_p (Ω cm ²)
LSFM	0.961	1.640	0.223	0.182
LSFM-Ru	0.961	2.084	0.172	0.112
LSFM-Co	0.962	2.034	0.176	0.123
LSFM-Fe	0.963	2.201	0.171	0.110
LSFM-Ni	0.963	1.879	0.177	0.119

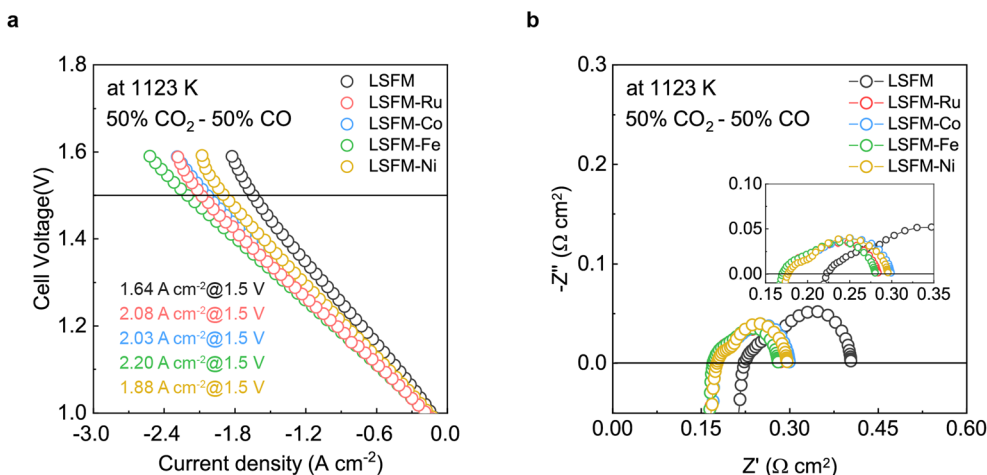


Fig. 4 (a) The CO₂ electrolysis performance with the infiltrated LSFM electrode feeding CO₂ : CO (50 : 50) at 1123 K. (b) Total impedance spectra of the cell with the infiltrated LSFM electrode at 1123 K.

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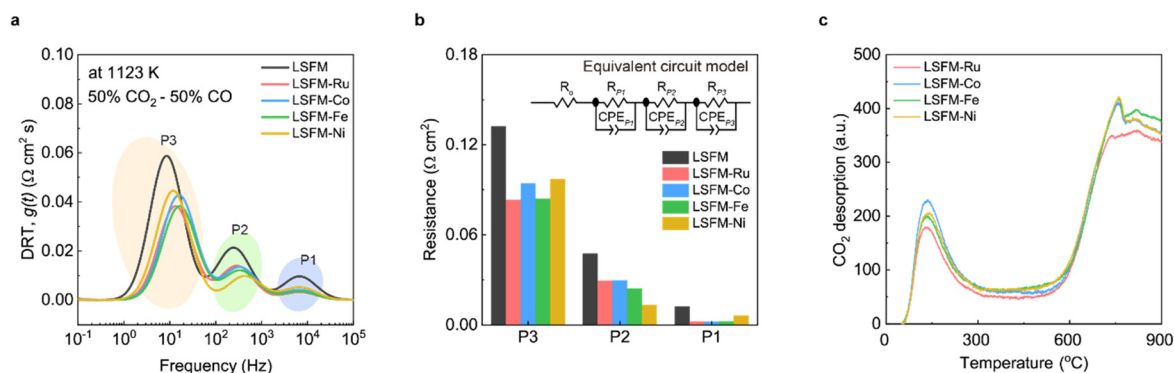


Fig. 6 (a) Comparison of plots of the distribution of relaxation times (DRT) for LSFM and the infiltrated LSFM electrodes at 1123 K. (b) Polarization resistance of each cell calculated from the circuit model fitting results, and (c) the CO₂-TPD profiles of the metal infiltrated LSFM.

oxygen electrodes of all the cells, the improvement of α and i_0 can mainly contribute to the metal-infiltrated fuel electrode.

To gain a deeper insight into the kinetics of the electrochemical reactions in metal-incorporated electrodes, the distribution of the relaxation time analysis was performed using the EIS data.³³ Fig. 6a shows the plots of the distribution of the relaxation time for the electrochemical processes for the electrodes at 1123 K in CO₂ electrolysis. The electrochemical process can be deconvoluted into three peaks (P1, P2, and P3), as shown in Fig. 6a. Specific peaks represent the rate-determining steps (RDSs) of the electrochemical reactions. P1 is concerned with the transfer of O²⁻ through the interface between the electrode and the LSGM electrolyte. P2 is correlated with the dissociation of the adsorbed CO₂ molecules into carbonate intermediates and CO. P3 is associated with the adsorption of CO₂ molecules onto the electrode surface.³⁴ For the LSFM electrode, the reactions in all the processes were enhanced by introducing a metal catalyst. To quantify the contribution of each process from the impedance results, an equivalent circuit model was used based on the distribution of the relaxation time analysis at 1123 K (Fig. 6b). The value of R_{P1} decreased

because of the improved interfacial stability between the electrode and electrolyte during infiltration. The value of R_{P1} of the LSFM-Ni electrode cell was higher than that of the other metal-infiltrated electrode cells. This was probably due to the slight reactivity with the electrolyte, which is consistent with the R_0 results of the impedance.³⁵ In the P2 process, the metal nanoparticle was strongly concerned with the dissociation process of the adsorbed CO₂ molecules by the donating electrons.³⁶ In our case, the Ni catalyst showed the best catalytic activity in the P2 process, followed by Ni > Fe > Ru ≥ Co. This may be attributed to the interaction between the metal particles and the carbonate intermediate on the LSFM electrode. Consequently, various factors caused by the catalytic activity of the metal particles, and the interaction between metal catalysts and perovskite oxides, should be considered when selecting the optimal catalyst. Because this is unclear, further studies on the use of SOECs are still required. For CO₂ electrolysis at the fuel electrode, CO₂ adsorption, which is the initial step in the electrochemical CO₂ reduction, is also important. In the subsequent P3 process, the Fe and Ru catalysts showed smaller peaks compared to the Co and Ni catalysts, suggesting that

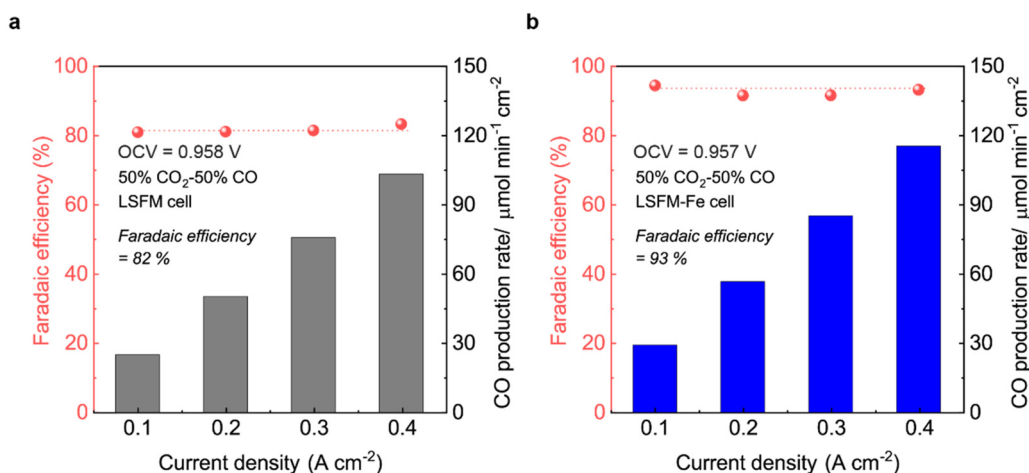


Fig. 7 Faradaic efficiency of the cell with (a) bare LSFM, and (b) LSFM-Fe electrode with a CO₂ : CO gas (50 : 50) mixture at 1123 K.



they had a stronger or more favorable impact on the adsorption behavior of CO₂. These comprehensive results suggest that appropriate metal catalysts should be explored from various perspectives, such as molecular adsorption and dissociation. In order to investigate the adsorption and desorption process in the metal-infiltrated electrodes for CO₂ reduction, CO₂-TPD was conducted as shown in Fig. 6c. The results obtained revealed the presence of two distinctive peaks at 373–573 K and 873–1173 K for all the electrodes. Interestingly, the Fe catalyst exhibited the strongest peak in the high-temperature range, which corresponds to the operating temperature of the SOECs. This finding indicates the superior performance of Fe catalyst at high temperatures, as it activates more active sites for CO₂ adsorption and dissociation.

Fig. 7 illustrates the FE of the LSFM and LSFM-Fe electrode cells under varying current densities. The FE can be calculated by the following equation by using the measured CO production rates in the composition of the gas outlets:

$$FE = \frac{n_{\text{CO,measured}}}{I \times n \times F} \times 100 (\%),$$

where I is the current density and $n_{\text{CO,measured}}$ is the measured CO production rates in the EC mode. The $n_{\text{CO,measured}}$ gradually increased as higher electrolysis currents were applied. The LSFM-Fe electrode exhibited a high FE at about 93%, which is attributed to the high surface activity of the metal catalyst, compared to the LSFM electrode with an FE of 83%. These results suggested that the Fe nanoparticles in the LSFM electrode have a good CO₂ reduction activity, making the LSFM-Fe electrode more efficient for CO₂ conversion.

Conclusions

In this study, we investigated the activity of various metal catalysts on LSFM fuel electrodes for the electrochemical oxidation of H₂, and CO₂ reduction. The Ru catalyst on the LSFM electrode had the best electrochemical performance (1.05 W cm² at 1073 K) with a low overpotential in the H₂ SOFC at 1073 K, which was approximately two-fold higher than that of the LSFM electrode (Ru > Ni > Fe ≥ Co). In the CO₂ electrolysis mode, the cell with the LSFM-Fe electrode achieved a current density of 2.201 A cm^{−2} at 1123 K when a voltage of 1.5 V (Fe > Ru ≥ Co > Ni) was applied. Unlike the hydrogen application, the Fe catalyst exhibited better catalytic activity and accelerated the electrode surface exchange kinetics better than Ru in CO₂ reduction, and this was found from the polarization resistance obtained by using EIS, and the high-exchange current density. In addition, the distribution of the relaxation time results provides insights into the activity of each metal catalyst in the electrochemical CO₂ reduction. Consequently, the Fe and Ru catalysts exhibited a higher adsorption of CO₂ molecules, which is the starting step of the CO₂ reduction. The LSFM-Ni electrode showed a higher catalytic activity than the LSFM-Fe and LSFM-Ru electrodes because of the interaction of the cata-

lyst with the carbonate intermediate and the LSFM structure. These results suggest that suitable metal catalysts should be explored from various perspectives, such as molecular adsorption and dissociation.

Conflicts of interest

There are no conflicts to declare.

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