Supplementary information

Activity switching of Sn and In species in Heusler alloys for electrochemical CO_2 reduction

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1. Experimental procedure

1.1 Material synthesis

Pure metal pieces (purity >99.9%) were alloyed by arc-melting. The obtained ingot was annealed under Ar atmosphere for homogenization and atomic ordering (Ni_2MnSn: 800 ˚C for 120 h, then 500 ˚C for 48 h; Ni_2MnIn: 1000 ˚C for 48 h, then 600 ˚C for 72 h). The annealed ingot was crushed by a pestle and mortar. For catalytic tests, the obtained powder was sieved to under 20 μm, and then annealed under a H_2 gas flow at 600 ˚C for 1 h to remove the strain introduced by crushing.

1.2 Physical characterization

Crystallographic characterization was performed by XRD using a Bragg-Brentano diffractometer with Cu-Kα radiation (Ultima IV, Rigaku). Relatively small peaks such as 111 and 200 peaks could be observed for an ordered structure while relatively large peaks, such as 220 and 400 peaks, were always observed even for a disordered structure (random occupation). Thus, the degree of ordering can be evaluated by comparison of experimental and theoretical intensity ratios for the small and large peaks. The theoretical values were calculated from the atomic scattering factors, including the anomalous dispersion terms,[1] with corrections using the multiplicity factor, and the Lorentz-polarization factor. The Debye-Waller factor due to thermal vibration was ignored, because its contribution was small, and because the factors for Sn and In having a low melting point for pure metals can be largely modified by forming Heusler alloys with a relatively high melting point. See the previous work for the details of ordered structure evaluation.[2]

Microstructures and chemical compositions of catalyst powders deposited on GDE were analyzed using field-emission scanning electron microscopy (FE-SEM; SU-70, Hitachi Hi-Tech) with energy dispersive X-ray spectroscopy (EDS). X-ray absorption spectroscopy

(XAS) was performed on the BL01B01 beamline at the SPring-8 at Japan Synchrotron Radiation Research Institute (JASRI). A double-crystal Si(111) monochromator was employed to obtain XAS data. The midpoint of the Sn K-edge XANES spectra or Sn-foil was set to 29195.2 eV for energy calibration of the Sn K-edge and In K-edge XANES spectra. The first peak in the Cu foil spectrum was set to 8980.3 eV for calibration of energy levels for measuring Ni and Mn K-edges XANES spectra. The XAS data were analyzed using the Demeter package.[3] High-angle annular dark field scanning TEM (HAADF-STEM) and corresponding EDX-mapping of the catalysts after electrolysis were performed on a Titan 3 60–300 Double Corrector (FEI-Company) equipped with a Super-X system at 200 kV.

1.3 Electrochemical measurement

For evaluation of the CO_2 reduction reaction (CO_2RR), HZ-7000 (Hokuto Denko) was used for measuring the electrocatalytic activity. All CO_2RR activities were measured in a CO_2 saturated 1 M $KHCO_3$ solution. $KHCO_3$ (Sigma, 99.7%) and ultrapure water (MilliQ, 18.2 MΩ) were used for preparation of electrolytes. A custom-made gas diffusion electrode setup was used for measuring the CO_2RR activity, as reported previously.[4, 5] A gas diffusion electrode (GDE, MFK-A (Mitsubishi Chemical Corp.)) modified with catalyst ink was employed as the working electrode. Carbon paper (Toray) and Ag/AgCl (sat. KCl) were used for counter and reference electrodes, respectively. Nafion 117 membrane (Sigma-Aldrich) was employed for separating the cathodic and anodic compartments. During measurement, CO_2 was continuously flowed at a rate of 10 mL/min. The CO_2RR activity for catalysts was measured under galvanostatic conditions for 30 min. For Ni_2MnIn, the CO_2RR activity was also measured using potentiostatic experiments. The average potential and current value were used to compare the CO_2RR activity of Ni_2MnIn measured by potentiostatic and galvanostatic experiments (Figure S3). The solution resistance (R_{sol}) for iR correction was

measured by electrochemical impedance spectroscopy (EIS). The metal concentration of metal elements in the electrolyte after electrolysis was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, ARCOS EOP (SPECTRO)).

For preparation of working electrodes, catalyst ink was sprayed onto GDEs (electrode area 1.89 cm^2) using an airbrush (HP-BS, ANEST IWATA). The catalyst ink was prepared by mixing catalysts (3 mg), Ketjen black (2 mg, EC600JD, Lion Corp.), 20 μL 5% Nafion (Sigma) and 300 μL ethanol (Wako) using an ultrasonic bath for 30 min on a pre-heated hot plate. As references, In (< 45 μm, Kojundo Chemical Laboratory Co., Ltd.) and Sn (< 38 μm, Kojundo Chemical Laboratory Co., Ltd.) powders were used.

Linear sweep voltammograms (LSV) for the hydrogen evolution reaction (HER) of Heusler alloy catalyst-loaded GDEs were measured at a scan rate of 5 mV/s in Ar-purged 1 M phosphate buffer solution (PBS) at pH = 7.6. The PBS was prepared from ultrapure water (Milli-Q, 18.2 MΩ), $NaH_2PO_4 \cdot 2H_2O$ and $Na_2HPO_4 \cdot 12H_2O$ (>99%, FUJIFILM Wako Chemicals). H-type glass-made cell, Pt-mesh, and a reversible hydrogen electrode (RHE) were used as the electrochemical cell, counter electrode, and reference electrode, respectively. The solution resistance (R_{sol}) for iR correction of LSVs was measured by electrochemical impedance spectroscopy (EIS).

1.4 Product analysis for carbon dioxide reduction

Gaseous CO_2RR products were analyzed using gas chromatography (GC). A GC-8A (Shimadzu) equipped with a thermal conductivity detector (TCD) and Shincarbon ST (Shinwa Chemical Industries) column was used for detecting H_2. A GC-8A equipped with a flame ionization detector (FID), methanizer (MTN-1, Shimadzu), and Shincarbon ST column was used for detecting carbon monoxide (CO). Argon (Ar) gas and N_2 gas were used as carrier gases for GC-TCD and TC-FID, respectively. Liquid CO_2RR products (e.g., formate)

were quantitatively analyzed by 1H-NMR (AVANCE III 600, 600 MHz, Bruker) using a pre-saturation method as described elsewhere.[4, 5] DMSO (Wako) was used as an internal standard.
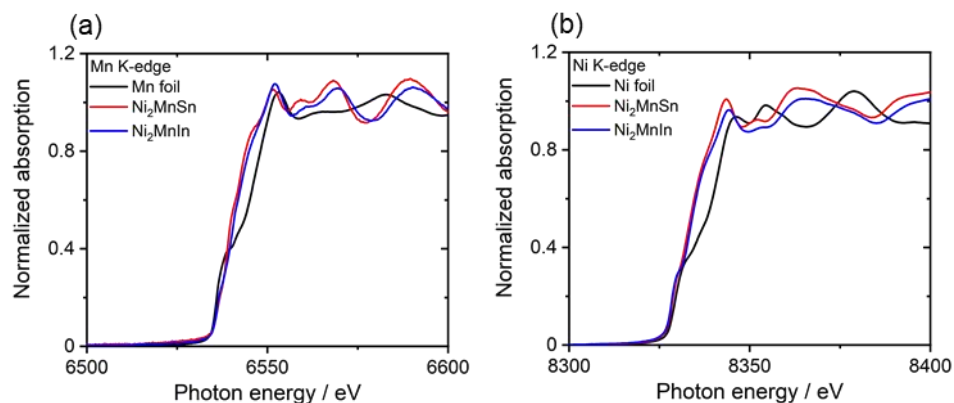
2.1 Supplemental figures and tables

Figure S1 (a) Mn K-edge and (b) Ni K-edge XANES spectra for Ni_2MnIn and Ni_2MnSn.

Table S1 Normalized elemental ratio (at%) for catalyst powders after spraying on gas diffusion electrodes, as analyzed by SEM-EDX. In or Sn species were used for normalization.

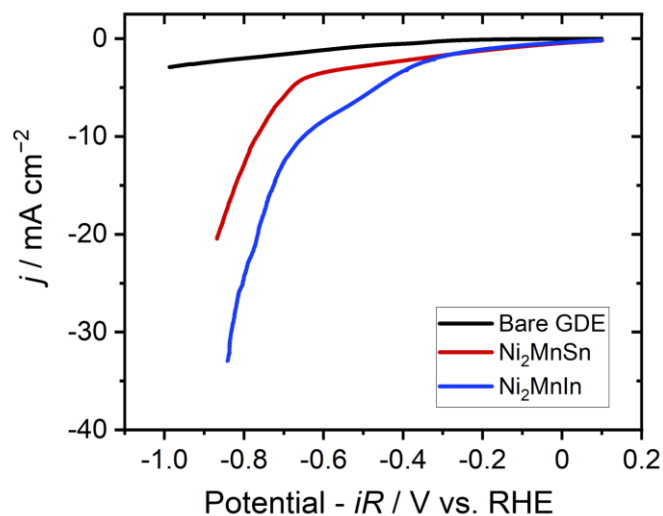| Sample	Ni	Mn	In	Sn
Ni_2MnIn	2.04	0.96	1.0	
Ni_2MnSn	1.97	0.94		1.0

Figure S2 Current density (j) versus potential (U) curves for bare GDE (black), Ni$_2$MnSn loaded GDE (red) and Ni$_2$MnIn (blue) measured in phosphate buffer solution (PBS, pH = 7.6) saturated with Ar. All measurements were iR-corrected.
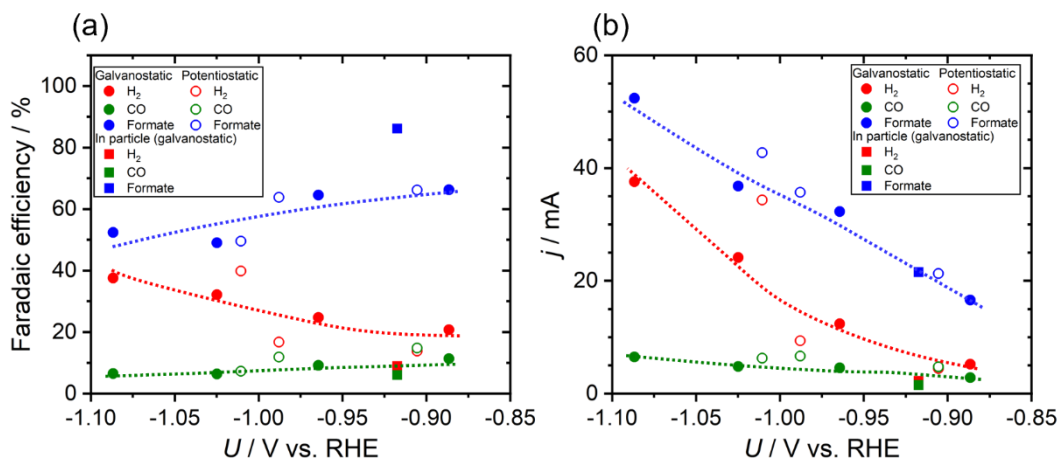

Figure S3 Comparison of CO$_2$RR activity for Ni$_2$MnIn evaluated by potentiostatic and galvanostatic experiments. (a) Faradaic efficiencies and (b) partial current density of CO$_2$RR products were plotted against applied potential (V versus reversible hydrogen electrode (RHE)). CO$_2$RR activity for In particle is also plotted as a reference. Dotted lines are guidelines. The potential value was iR-corrected.

Table S2 Concentration of metal elements after electrolysis determined by ICP-OES analysis. The unit is ppm. The number in parentheses gives the ratio of the amount of the metal elements leached into the solution to the amount loaded onto the electrode.

Catalyst	Element	25 mA	50 mA	75 mA	100 mA
Ni_2MnIn	Ni	0.16 (0.10%)	0.17 (0.11%)	0.15 (0.10%)	0.13 (0.08%)
	Mn	0.26 (0.37%)	0.33 (0.46%)	0.25 (0.35%)	0.20 (0.27%)
	In	0.10 (0.07%)	0.09 (0.06%)	0.08 (0.05%)	< 0.07 $(< 0.05\%)^a$

Catalyst	Element	25 mA	50 mA	75 mA	100 mA
Ni_2MnSn	Ni	0.04 (0.03%)	0.04 (0.03%)	0.03 (0.02%)	0.08 (0.05%)
	Mn	0.10 (0.14%)	0.06 (0.08%)	0.04 (0.06%)	0.15 (0.21%)
	Sn	n.d. $(-)^b$	n.d. $(-)^b$	n.d. $(-)^b$	n.d. $(-)^b$

a: The concentration was so low to determine the accurate value.

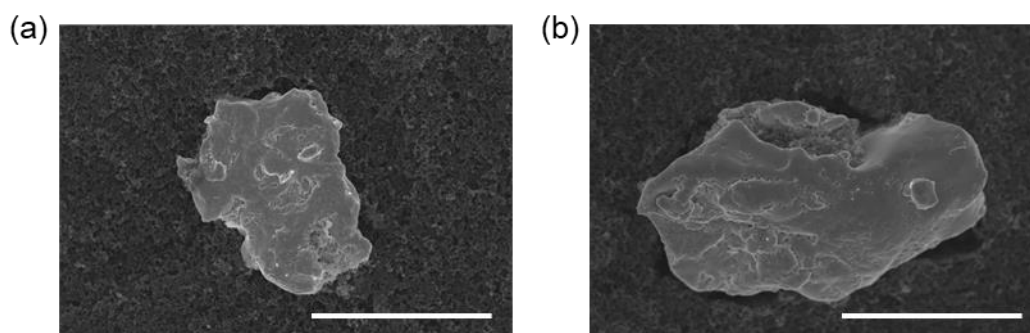b: Not detected (under detection limit).

Figure S4 Representative SEM images of a catalyst powders after electrolysis (constant current at 25mA). (a) Ni_2MnIn and (b) Ni_2MnSn. Scale bar: 5 μm.

Table S3 Normalized elemental ratio (at%) for catalyst powders after electrolysis (at 25mA), as analyzed by SEM-EDX. In or Sn species were used for normalization.

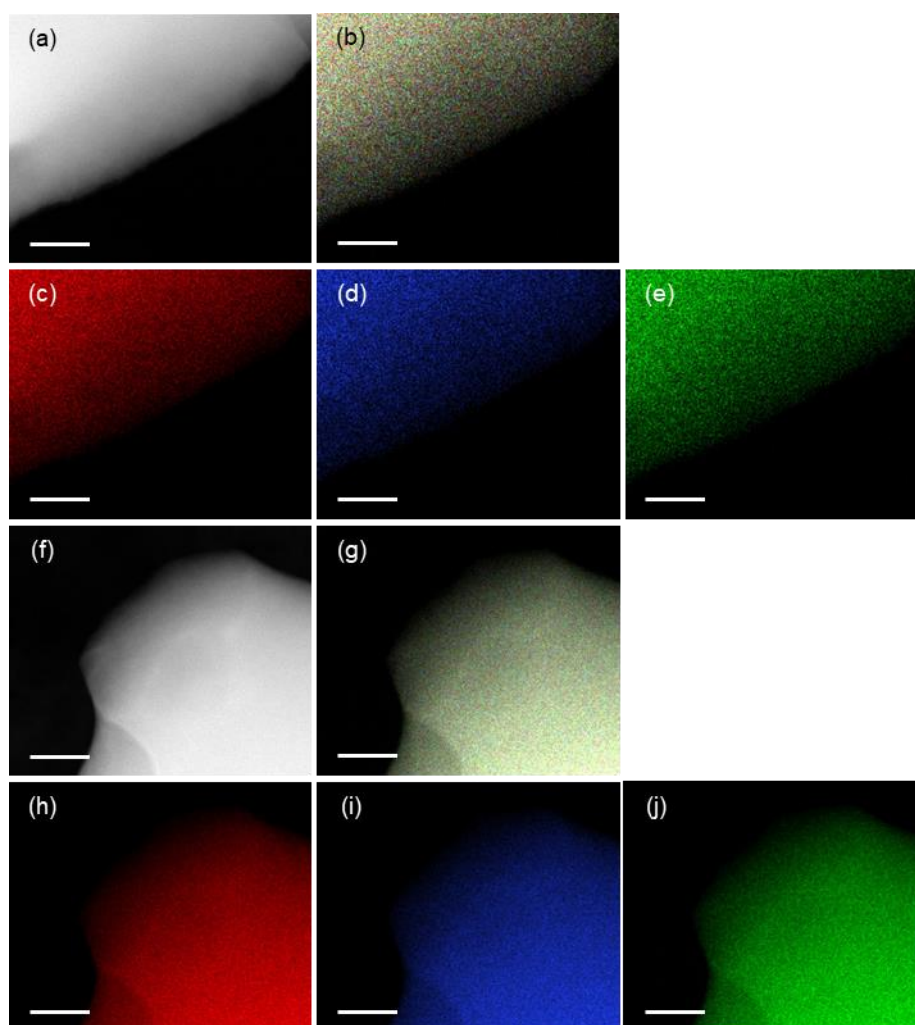| Sample	Ni	Mn	In	Sn
Ni_2MnIn	2.07	0.94	1.0	-
Ni_2MnSn	1.96	0.93	-	1.0

Figure S5. STEM image and EDX-mapping of (a-e) Ni_2MnIn and (f-g) Ni_2MnSn after electrolysis (constant current at 25mA). (a, f) HAADF-STEM image and (b-e, g-j) EDX mapping. (b, g) merge (c, h) Ni, (d, i) Mn, (e) In and (j) Sn. Scale bar: 50 nm.

References

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2. T. Kojima, S. Kameoka and A. P. Tsai, *ACS Omega*, 2017, **2**, 147-153.
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4. K. Iwase, T. Hirano and I. Honma, *ChemSusChem*, 2022, **15**, e202102340.
5. Y. Wu, K. Iwase, T. Harada, S. Nakanishi and K. Kamiya, *ACS Appl. Nano Mater.*, 2021, **4**, 4994-5003.