# Supporting Information

## Developing a series of calcium-doped pyrochlore iridates for the oxygen evolution reaction in PEM water electrolysis

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### X-ray fluorescence (XRF) analysis

Several elements could not be excluded from the measurement. Since especially phosphorous had a large wt% (likely originating from the sample holder materials), the weight percentages measured by the device do not represent the real wt% of the metals in the sample. To account for this, the measured weight percentages of the three metals were put into relation of their sum, excluding the weight percentages of the other elements.

$$wt\%(metal)_{meas} = \frac{wt\%(metal)_{XRF}}{wt\%(Pr)_{XRF} + wt\%(Ca)_{XRF} + wt\%(Ir)_{XRF}} \cdot 100\,\%$$

$$wt\%(Pr)_{theo} = \frac{(2-x) \cdot M(Pr)}{(2-x) \cdot M(Pr) + x \cdot M(Ca) + 2 \cdot M(Ir)} \cdot 100\,\%$$

$$wt\%(Ca)_{theo} = \frac{x \cdot M(Ca)}{(2-x) \cdot M(Pr) + x \cdot M(Ca) + 2 \cdot M(Ir)} \cdot 100\,\%$$

$$wt\%(Pr)_{theo} = \frac{2 \cdot M(Ir)}{(2-x) \cdot M(Pr) + x \cdot M(Ca) + 2 \cdot M(Ir)} \cdot 100\,\%$$

### Brunauer-Emmett-Teller (BET) analysis

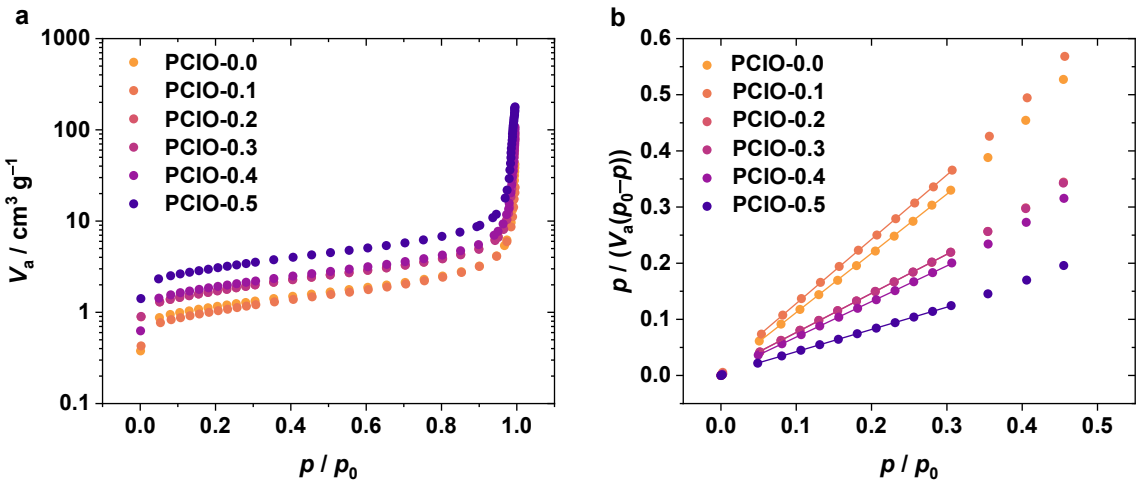


**Figure S 1**: Nitrogen adsorption isotherms (a) and BET analysis (b).

## Scanning electron microscopy (SEM) images

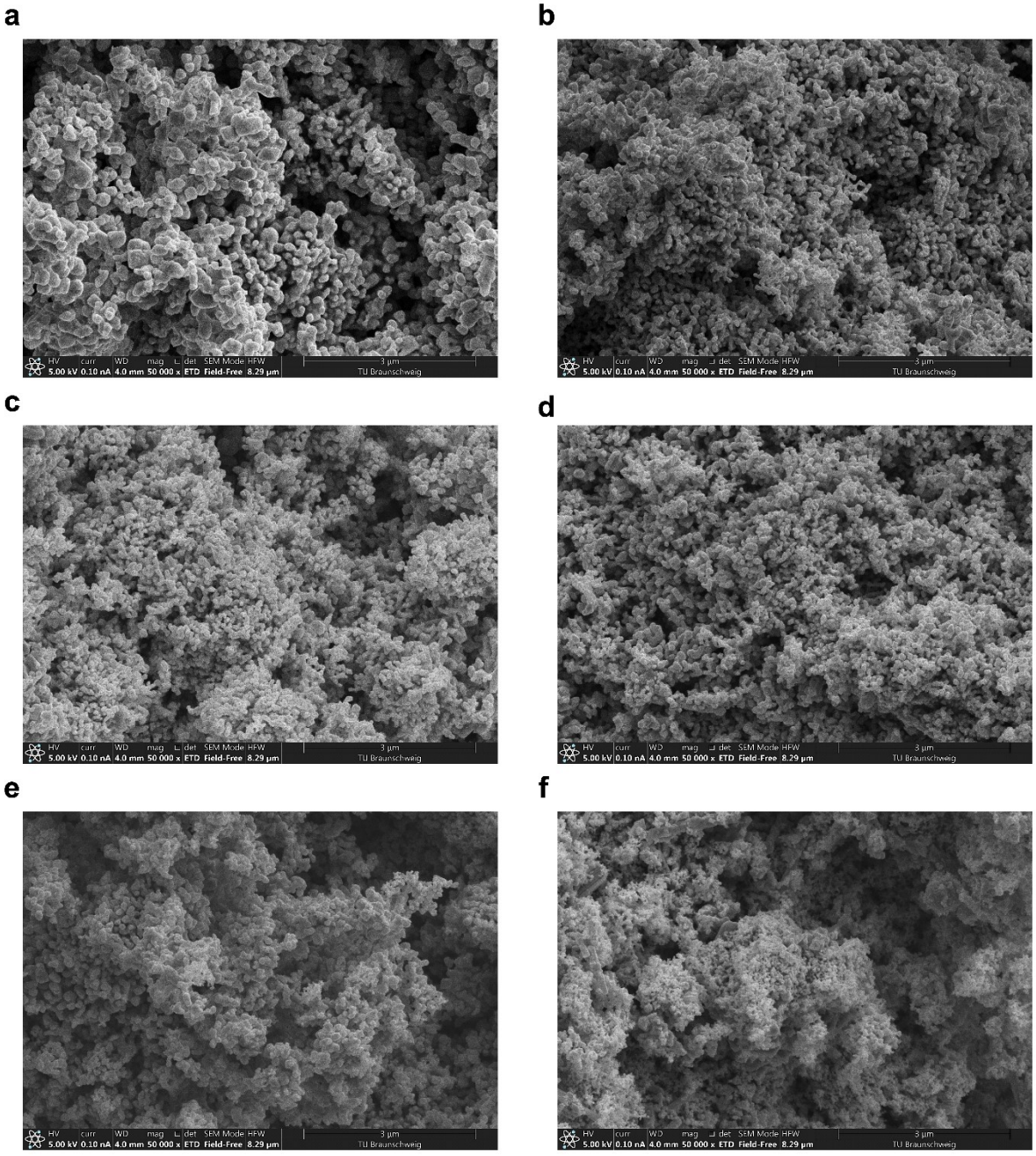


**Figure S 2**: SEM images of the PCIO materials: a) PCIO-0.0, b) PCIO-0.1, c) PCIO-0.2, d) PCIO-0.3, e) PCIO-0.4, f) PCIO-0.5.

**SEM energy dispersive X-ray spectroscopy (SEM-EDX) images**

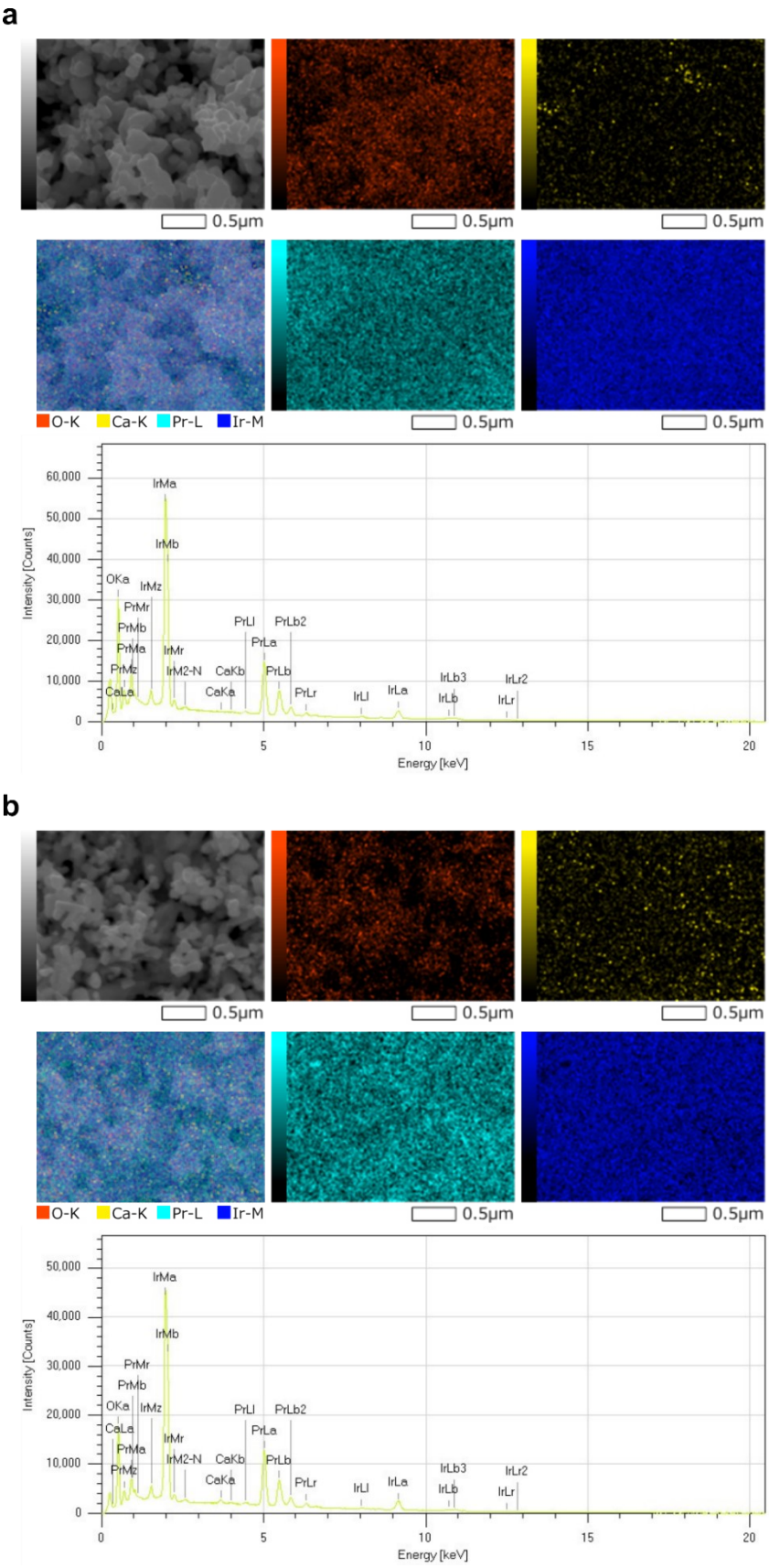


**Figure S 3:** SEM-EDX elemental mapping and intensities: a) PCIO-0.0, b) PCIO-0.1, c) PCIO-0.2, d) PCIO-0.3, e) PCIO-0.4, f) PCIO-0.5. Elemental distribution maps are presented with ZAF correction applied. For PCIO-0.0, the CaKα signal can barely discriminated from the background, so the elemental mapping represents only traces of Ca in the sample.

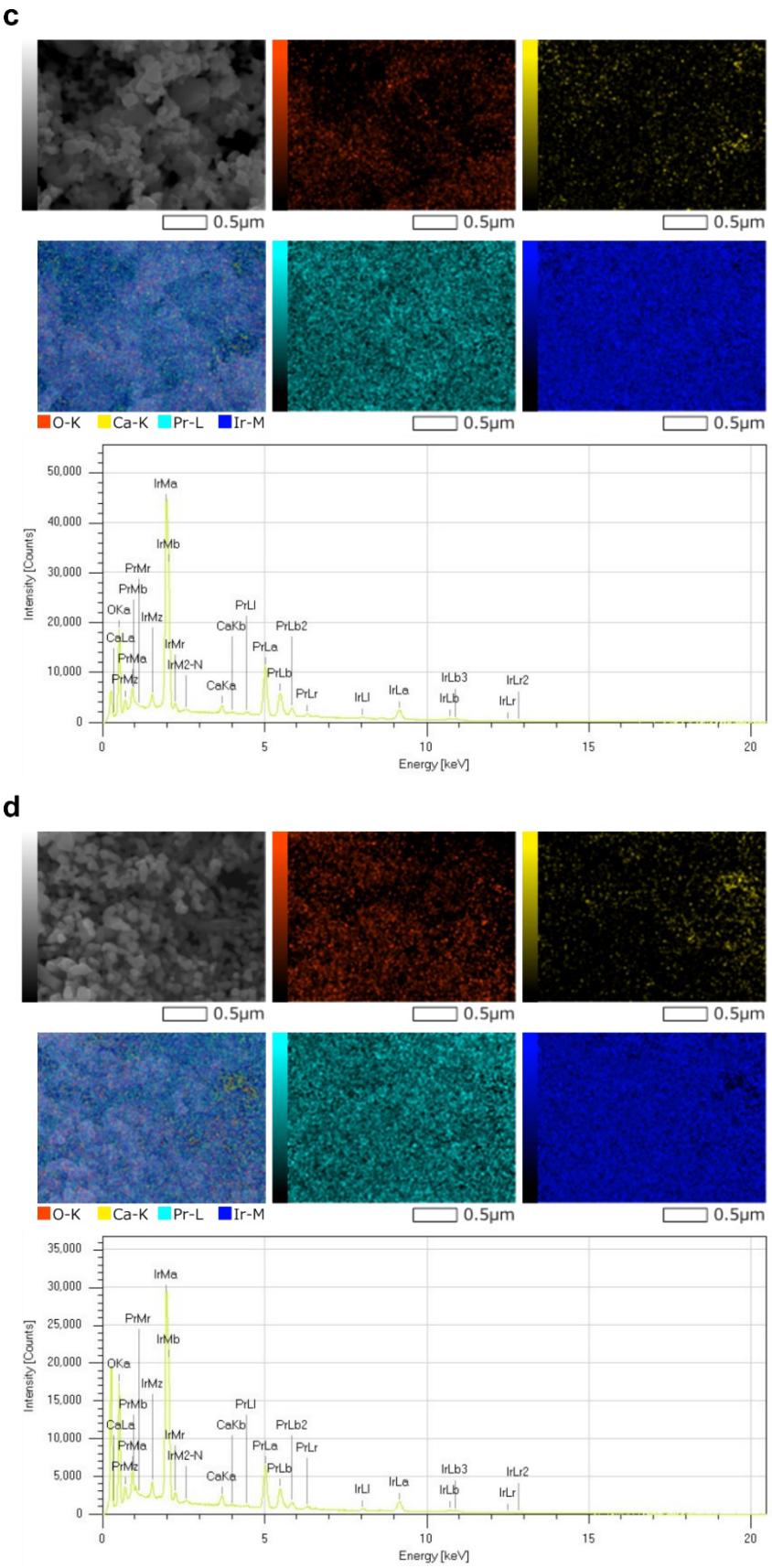


**Figure S 3:** (Continued.)

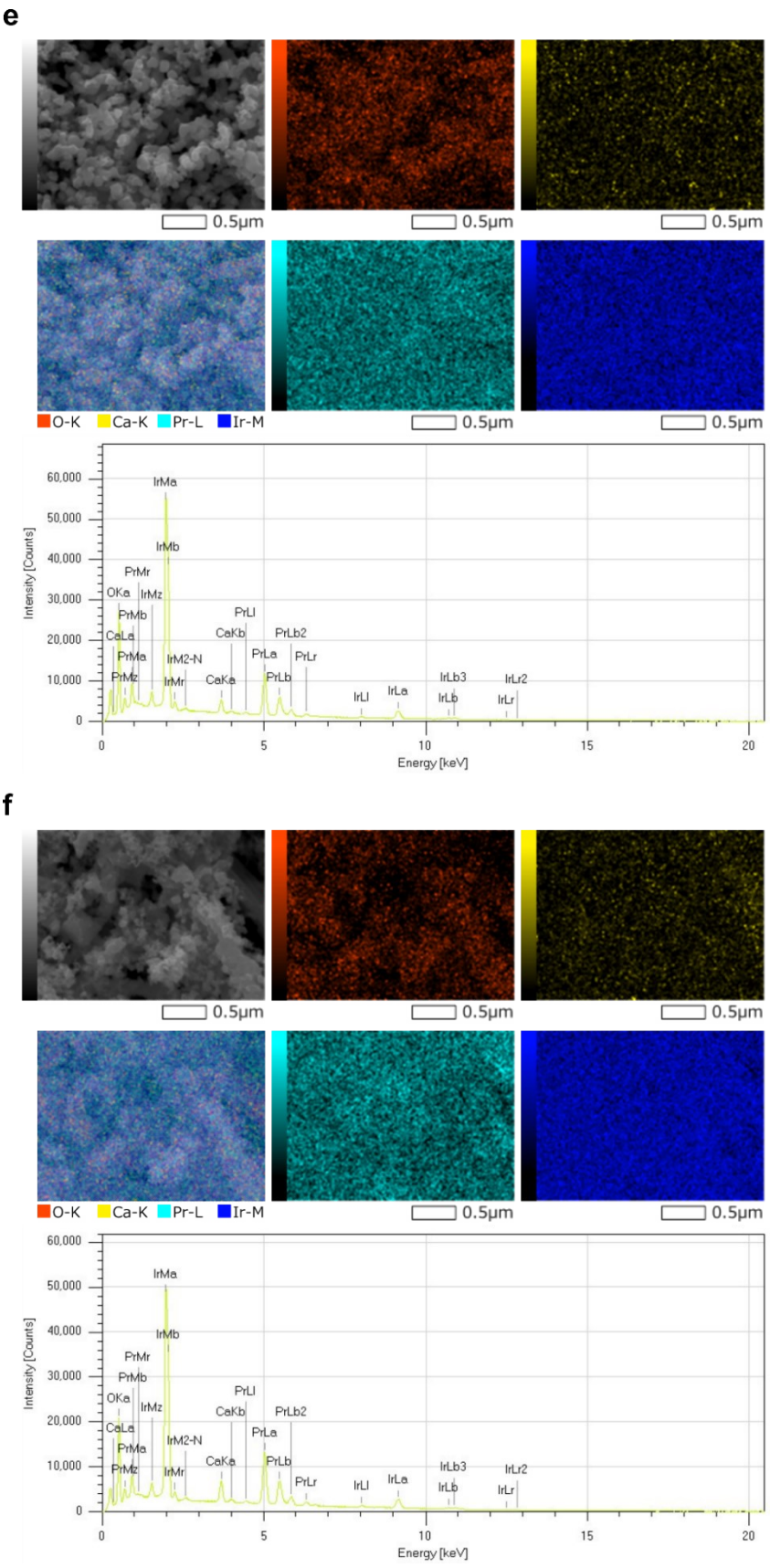


**Figure S 3:** (Continued.)

**X-ray Photoelectron Spectroscopy (XPS) spectra of Ir 4f region**

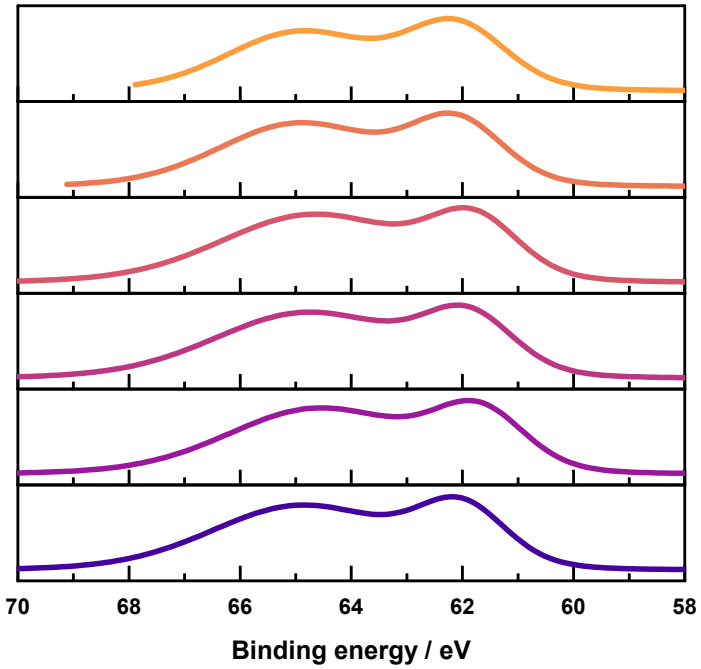


**Figure S 4:** High-resolution XPS spectrum of the Ir 4f region

**Determination of the electrochemically active surface area (ECSA)**

The electrochemically active surface area was determined by measuring cyclic voltammograms at different scan rates in the non-Faradaic region. The modulus of the current was averaged between forward and backward scan and plotted against the scan rate. The ECSA was determined from the double layer capacity given by the slope, the catalyst loading of $m_{cat}$ = 50 µg and the specific capacitance usually given as $C_S$ = 60 µF/cm².[1,2]

$$ECSA = \frac{C_{DL}}{C_s \cdot m_{cat}}$$

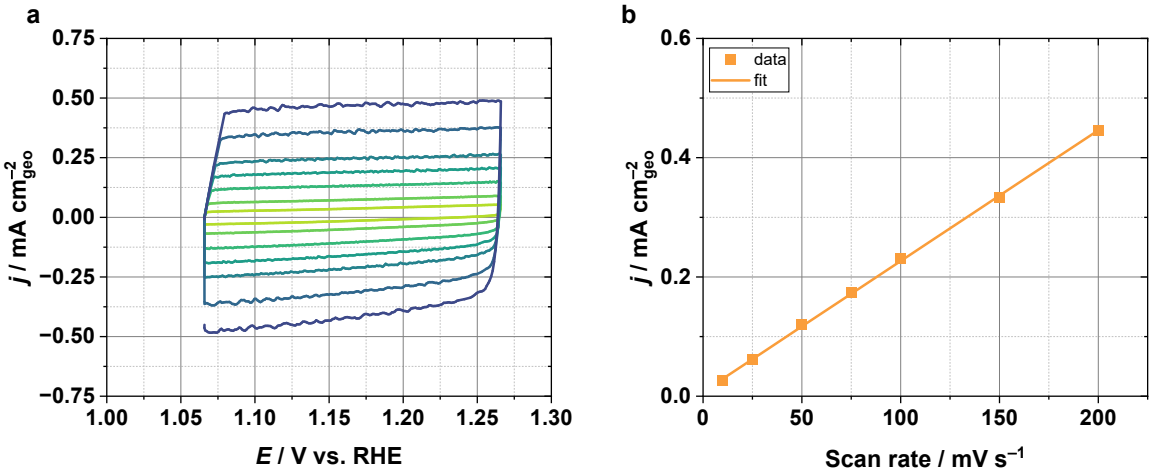


**Figure S 5:** ECSA determination of PCIO-0.0: a) CVs at different scan rates in non-Faradaic region, b) charging current density at 1.166 V vs. RHE (0.90 V vs. Ag/AgCl 3M KCl) against scan rate.

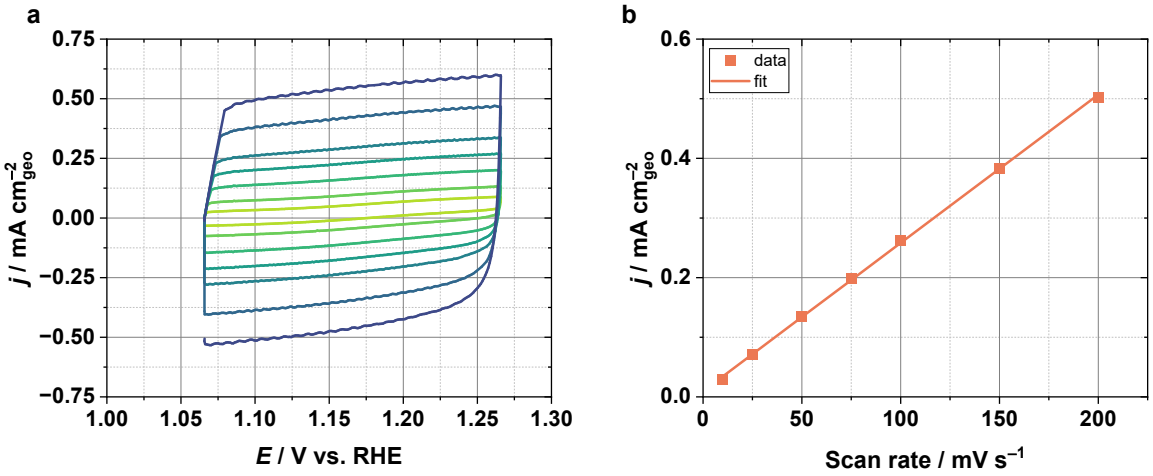


**Figure S 6:** ECSA determination of PCIO-0.1: a) CVs at different scan rates in non-Faradaic region, b) charging current density at 1.166 V vs. RHE (0.90 V vs. Ag/AgCl 3M KCl) against scan rate.

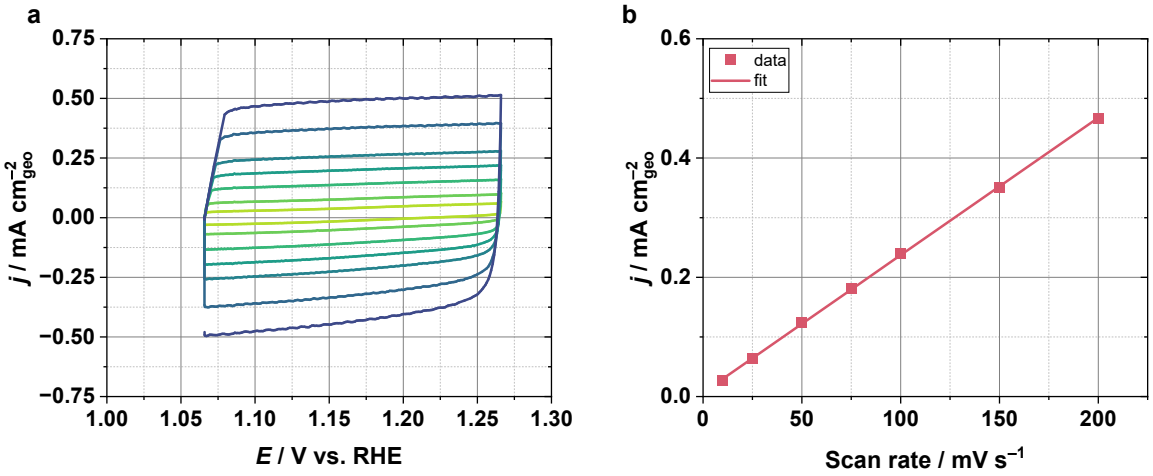


**Figure S 7:** ECSA determination of PCIO-0.2: a) CVs at different scan rates in non-Faradaic region, b) charging current density at 1.166 V vs. RHE (0.90 V vs. Ag/AgCl 3M KCl) against scan rate.

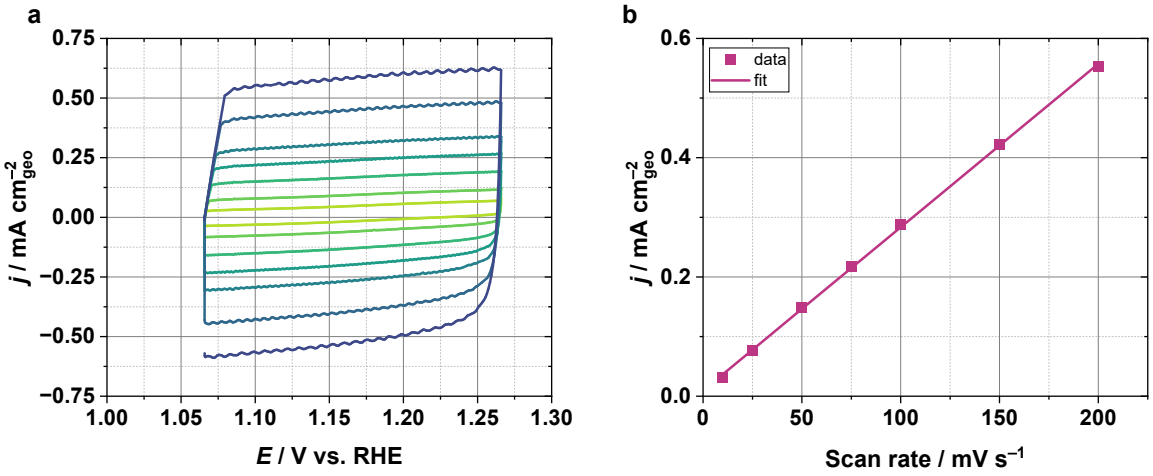


**Figure S 8:** ECSA determination of PCIO-0.3: a) CVs at different scan rates in non-faradaic region, b) charging current density at 1.166 V vs. RHE (0.90 V vs. Ag/AgCl 3M KCl) against scan rate.

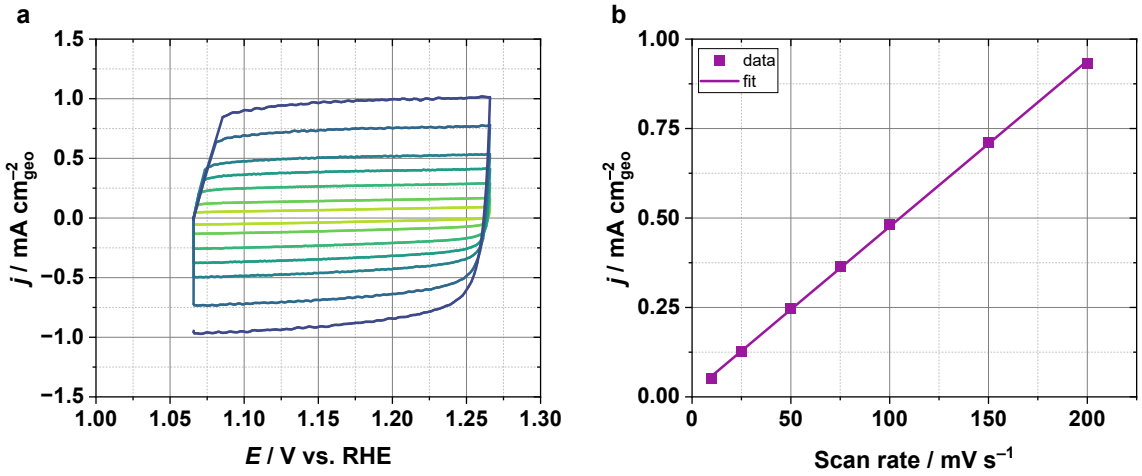


**Figure S 9:** ECSA determination of PCIO-0.4: a) CVs at different scan rates in non-Faradaic region, b) charging current density at 1.166 V vs. RHE (0.90 V vs. Ag/AgCl 3M KCl) against scan rate.

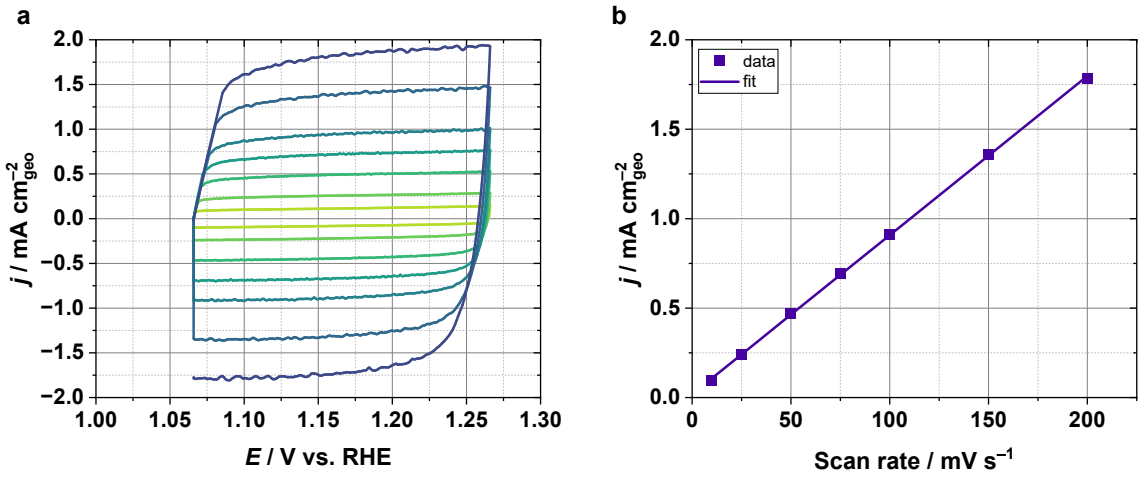


**Figure S 10:** ECSA determination of PCIO-0.5: a) CVs at different scan rates in non-Faradaic region, b) charging current density at 1.166 V vs. RHE (0.90 V vs. Ag/AgCl 3M KCl) against scan rate.

**Determination of the S-number**

The stability number was determined by assuming 100 % Faradaic efficiency. The amount of oxygen evolved was calculated from the charge transferred during the 10 cyclovoltammetry cycles as well as the 60 min chrono potentiometric holds. The amount of iridium dissolved was determined via ICP-MS. Shown below is an exemplary calculation for PCIO-0.5.

$$n_{O_2}^{evolved} = \frac{\int_0^t i\,dt}{Fn} = \frac{1.051\ C\ (from\ CV)\ +\ 1.963\ mA\ \cdot\ 3600\ s\ (from\ CP)}{96485\ \frac{C}{mol}\ \cdot\ 4} = 2.103\ \cdot\ 10^{-5}\ mol$$

$$n_{Ir}^{dissolved} = \frac{c_{Ir}\ \cdot\ V}{M_{Ir}} = \frac{10.82\ \mu g/L\ \cdot\ 0.0090\ L}{192.217\ g/mol} = 5.065\ \cdot\ 10^{-10}\ mol$$

$$S - number\ = \frac{n_{O_2}^{evolved}}{n_{Ir}^{dissolved}} = \frac{2.103\ \cdot\ 10^{-5}\ mol}{5.065\ \cdot\ 10^{-10}\ mol} = 4.15\ \cdot\ 10^{4}$$

**Table S 1:** Comparison of environment, electrolyte, testing conditions and ionomer content for the S-numbers of catalysts compared within this work.

| Reference | Environment | Electrolyte | Catalyst | Testing conditions | Ionomer content | S-number |
|---|---|---|---|---|---|---|
| **Geiger et al.**[3] | SFC | 0.1 M $HClO_4$ | $IrO_2$ | 5 mV/s sweep to 1.8 V | 4.3 wt% | ~$2.0 \cdot 10^6$ |
| **Geiger et al.**[3] | SFC | 0.1 M $HClO_4$ | $IrO_x$ | 5 mV/s sweep to 1.65 V | 40.5 wt% | ~$1.0 \cdot 10^5$ |
| **Geiger et al.**[3] | SFC | 0.1 M $HClO_4$ | Ir metal | 5 mV/s sweep to 1.55 V | 40.5 wt% | ~$1.0 \cdot 10^5$ |
| **Geiger et al.**[3] | SFC | 0.1 M $HClO_4$ | $Ba_2PrIrO_6$ | 5 mV/s sweep to 1.65 V | 40.5 wt% | ~$3.0 \cdot 10^4$ |
| **Chen et al.**[4] | RDE | 0.1 M $HClO_4$ | $IrO_2$ | 10 mA/$cm^2_{geo}$ 180 min | 14 wt% | ~$1.0 \cdot 10^5$ |
| **Chen et al.**[4] | RDE | 0.1 M $HClO_4$ | Ir metal | 10 mA/$cm^2_{geo}$ 180 min | 14 wt% | ~$5.0 \cdot 10^4$ |
| **Chen et al.**[4] | RDE | 0.1 M $HClO_4$ | $SrCo_{0.9}Ir_{0.1}O_{3\ \delta}$ | 10 mA/$cm^2_{geo}$ 180 min | 14 wt% | ~$8.0 \cdot 10^4$ |
| **Edgington et al.**[5] | Steady state cell | 0.1 M $HClO_4$ | $IrO_x$ | 20 mV/s sweep to 1.7 V<br>1.7 V hold 10 min<br>20 mV/s sweep to OCV<br>repeat | 8 – 16 wt% | $2.3 \cdot 10^5$ |
| **Edgington et al.**[5] | Steady state cell | 0.1 M $HClO_4$ | $SrIr_{0.8}Zn_{0.2}O_3$ | 20 mV/s sweep to 1.7 V<br>1.7 V hold 10 min<br>20 mV/s sweep to OCV<br>repeat | 8 – 16 wt% | $3.2 \cdot 10^5$ |
| **Zhang et al.**[6] | Steady state cell | 0.1 M $HClO_4$ | $H_{3.6}IrO_4$ 3.7 $H_2O$ | 1 mA/$cm^2_{oxide}$ (15 mA/$cm^2_{geo}$)<br>60 min | N/A | ~$1.5 \cdot 10^5$ |
| **Zhang et al.**[6] | Steady state cell | 0.1 M $HClO_4$ | $H_{3.5}IrO_4$ | 1 mA/$cm^2_{oxide}$ (11 mA/$cm^2_{geo}$)<br>60 min | N/A | ~$1.3 \cdot 10^5$ |
| **Zhang et al.**[6] | Steady state cell | 0.1 M $HClO_4$ | 6H-$SrIrO_3$ | 1 mA/$cm^2_{oxide}$ (5 mA/$cm^2_{geo}$)<br>60 min | N/A | ~$2.2 \cdot 10^4$ |
| **Zhang et al.**[6] | Steady state cell | 0.1 M $HClO_4$ | $Sr_2Ir_{0.5}Fe_{0.5}O_4$ | 1 mA/$cm^2_{oxide}$ (3.5 mA/$cm^2_{geo}$)<br>60 min | N/A | ~$2.0 \cdot 10^3$ |
| **This work** | RDE | 0.1 M $HClO_4$ | PCIO-0.0 | 10 x 20 mV/s cycling (1.066 – 1.766 V)<br>10 mA/$cm^2_{geo}$ 60 min | 14 wt% | $1.81 \cdot 10^4$ |
| **This work** | RDE | 0.1 M $HClO_4$ | PCIO-0.1 | 10 x 20 mV/s cycling (1.066 – 1.766 V)<br>10 mA/$cm^2_{geo}$ 60 min | 14 wt% | $1.80 \cdot 10^4$ |
| **This work** | RDE | 0.1 M $HClO_4$ | PCIO-0.2 | 10 x 20 mV/s cycling (1.066 – 1.766 V)<br>10 mA/$cm^2_{geo}$ 60 min | 14 wt% | $2.62 \cdot 10^4$ |
| **This work** | RDE | 0.1 M $HClO_4$ | PCIO-0.3 | 10 x 20 mV/s cycling (1.066 – 1.766 V)<br>10 mA/$cm^2_{geo}$ 60 min | 14 wt% | $3.12 \cdot 10^4$ |
| **This work** | RDE | 0.1 M $HClO_4$ | PCIO-0.4 | 10 x 20 mV/s cycling (1.066 – 1.766 V)<br>10 mA/$cm^2_{geo}$ 60 min | 14 wt% | $3.56 \cdot 10^4$ |
| **This work** | RDE | 0.1 M $HClO_4$ | PCIO-0.5 | 10 x 20 mV/s cycling (1.066 – 1.766 V)<br>10 mA/$cm^2_{geo}$ 60 min | 14 wt% | $4.15 \cdot 10^4$ |

## References


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