

The importance of water structure and catalyst-electrolyte interface on the design of water splitting catalysts

Ronguang Zhang, Paul E. Pearce, Yan Duan, Nicolas Dubouis, Thomas Marchandier and Alexis Grimaud*

Supporting materials

Electrochemical measurements

Electrochemical measurements were carried out at room temperature using a VMP-300 potentiostat (Biologic Co., Claix, France). A conventional three-electrode configuration was used: a glassy carbon electrode (Pine) with geometric surface area of 0.196 cm² as the working electrode, a saturated single junction Ag/AgCl electrode (Hach-Lange) with a potential of 200 mV vs. SHE as the reference electrode, and a Pt wire as the counter electrode. The reference electrode was regularly calibrated versus a reversible hydrogen electrode (Gaskatel). The CV measurements were performed between 0.76 and 1.7 V vs. RHE in 0.1 M HClO₄ electrolyte at a scan rate of 10 mVs⁻¹ with a rotating speed of 1600 rpm. Potentials are corrected with iR drop and reported versus RHE. Currents are scaled with the specific surface area of the perovskite catalysts measured by BET as shown in Table S1. The catalysts were drop-casted onto the working electrode. The drop-casting ink was prepared by dispersing 10 mg catalyst powders and 2 mg ethylene black carbon (Alfa Aesar 99.9%) in 1.940 mL of tetrahydrofuran (THF; Sigma-Aldrich 99.9%) and 0.060 mL of Nafion binder (5% weight, Ion Power). The loading of active material was 50 µg (10 µL ink) per electrode.

Table S1. BET specific surface areas measured or extracted from previous papers.

Sample name	Specific surface area (m ² /g)
IrO ₂	28 (ref 56)
Bi ₂ Ir ₂ O ₇	30 (ref 52)
Y ₂ Ir ₂ O ₇	21 (ref 52)
Li-IrO _x	27 (ref 57)
SrIrO ₃	1.14 (ref 51)
IrNi _{0.9} O _x	72 (ref 58)
Sr ₂ FeIrO ₆	0.70
Sr ₂ IrCoO ₆	0.97
Ba ₂ PrIrO ₆	0.45
La ₂ LiIrO ₆	1.7

UV-Vis spectroscopy

A suitable amount of materials was soaked to dissolve in 1 M HClO₄, 1 M H₂SO₄, 1 M HCl for 24 h. The solution was then centrifuged to remove undissolved solids. The resulted solutions were measured using a MettlerToledo UV5Bio spectrophotometer with using a UV cell with a path length of 1 cm.

Experimental procedure for the deposition of IrO_x

A suitable amount of Sr₂IrCoO₆ was soaked to dissolve in 1 M HClO₄ or 1 M H₂SO₄ for 24 h. The solution was then centrifuged to remove undissolved solids. The solution had a pink-purple color, proven to contain soluble iridium species as detailed in the previous paper. The solution was then diluted into 0.1 M HClO₄ (or 0.1 M H₂SO₄ for that dissolved in 1 M H₂SO₄) and was used as electrolytes for the deposition of IrO_x. The experimental set-up of the deposition is shown in Figure 5a of the main manuscript, and consists of a conventional three-electrode configuration. For the deposition, blank glassy carbon electrodes were cycled from 0.76 and 1.7 V vs. RHE with a scan rate of 10 mV/s in the 0.1 M HClO₄ (or 0.1 M H₂SO₄) electrolyte containing soluble iridium species as described above.

Operando X-ray diffraction collected for H_{3.4}IrO₄

Operando XRD measurements were performed in a BRUKER D8 Advance diffractometer with Cu K α radiation ($\lambda_{K\alpha 1} = 1.54056 \text{ \AA}$, $\lambda_{K\alpha 2} = 1.54439 \text{ \AA}$) using a home designed three-electrode cell. The working electrode was composed of a carbon gas diffusion layer (GDL, Quintech H2315 / H23) loaded with $\sim 9 \text{ mg}\cdot\text{cm}^{-2}_{\text{geo}}$ of H_{3.4}IrO₄ catalyst. The reference electrode was a 6 mm, single junction, saturated Ag/AgCl electrode. A carbon rod was used as counter electrode. A 0.1 M HClO₄ solution was used as electrolyte and the electrodes were left to soak prior to the experiment in order to fully wet the GDL. The material was initially discharged galvanostatically at a current of -0.95 mA to a voltage limit of 0.2 V vs RHE before being charged at a current of 0.95 mA until the potential stabilized at 1.414 V vs RHE. The XRD patterns were collected every 4 minutes which corresponds to steps of 0.06 in proton stoichiometry.

Table S2. Data used and extracted from the ref 83 for the activation energy of perovskites and corresponding current density.

	$\log i$ (A/cm ²) at $\eta = 0.3$ V	i (mA/cm ²) at $\eta = 0.3$ V	ΔE (kcal/mol)	ΔE (kJ/mol)
LaNiO ₃	-4.9048	7.41	17.2	71.96
LaCoO ₃	-5.869	2.83	19.5	81.59
La _{0.9} Sr _{0.1} CoO ₃	-5.2262	5.37	18.8	78.66
La _{0.6} Sr _{0.4} CoO ₃	-5.0298	6.54	18.1	75.73
La _{0.9} Ce _{0.1} CoO ₃	-5.8274	2.95	19.5	81.59
La _{0.9} Th _{0.1} CoO ₃	-5.619	3.63	20.5	85.77
Nd _{0.9} Sr _{0.1} CoO ₃			18.3	76.57
Gd _{0.9} Sr _{0.1} CoO ₃			22.4	93.72
La _{0.7} Sr _{0.3} FeO ₃	-6.3155	1.81	22	92.05
La _{0.5} Sr _{0.5} FeO ₃	-6.1131	2.21	21	87.86
LaMnO ₃	-7.3035	0.67	23.5	98.32
La _{0.9} Sr _{0.1} MnO ₃	-7.244	0.71	22.6	94.56
La _{0.6} Sr _{0.4} MnO ₃	-6.8988	1.00	22.1	92.47
La _{0.8} K _{0.2} MnO ₃	-6.7976	1.12	23.1	96.65
La _{0.8} Ca _{0.2} MnO ₃	-6.4762	1.54	22.5	94.14
La _{0.8} Sr _{0.2} CrO ₃	-7.5356	0.53	25.7	107.53

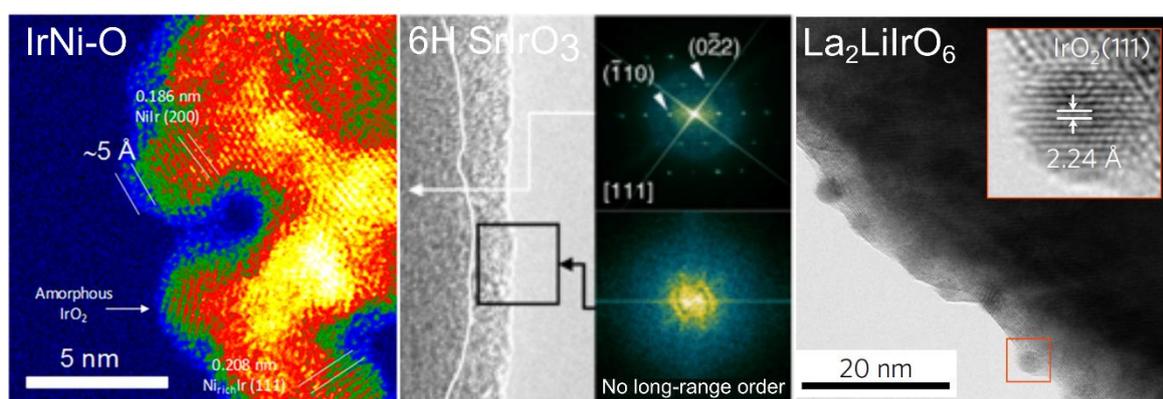


Figure S1. High resolution TEM images showing the formation of amorphous IrO_x layer on the surface of Ir-Ni mixed oxide (left) and 6-H SrIrO₃ (middle) while crystalline IrO₂ were found on the surface of La₂LilrO₆ after cycling (right). Figures taken from the ref 58, 51, and 44 with permission.