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Electronic Supplementary Information (ESI)

A two-dimensional perovskite oxyfluoride $Pb_3Fe_2O_5F_2$ as a catalyst for electrochemical oxidation of water to oxygen

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Experimental

Synthesis of $Pb_3Fe_2O_5F_2$ and $PbFeO_2F$

In accordance with a previous report,[1] $Pb_3Fe_2O_5F_2$ powder was synthesized through a solid-state reaction in vacuum. A mixture of PbO (99.9%, Rare Metallic Co. Ltd.), PbF_2 (99.9%, Mitsuwa Pure Chemical), and α-Fe_2O_3 (99.9%, FUJIFILM Wako Pure Chemical) powders, prepared in the ratio (molar basis) PbO:PbF_2:α-Fe_2O_3 = 2:1:1, was wrapped in a Pt sheet and then heated at 873 K for 12 hours in an evacuated Pyrex tube.

$PbFeO_2F$ powder was synthesized through a solid-state reaction at high pressure, using a mixture of PbO (99.9%, Kanto Chemical), PbF_2 99.999%, Soekawa Chemical) and Fe_2O_3 (99.99%, Rare Metallic).[2] A stoichiometric mixture of the starting materials was dried overnight by evacuating at ca. 573 K. The mixture was sealed in a gold capsule (0.2 mm thick, 3.1 mm inner diameter, and 3.2 mm depth), which was placed in a NaCl sleeve. The sample was then inserted into a pyrophyllite cube block (one side 13 mm) with a cylindrical graphite heater. The mixture was allowed to react in a TRY cubic multianvil-type high pressure apparatus (NAMO 2001) at 6.0 GPa and 1173 K for 30 min and then was quenched to room temperature.

The single-phase production of $PbFeO_2F$ and $Pb_3Fe_2O_5F_2$ was confirmed by X-ray diffraction (XRD).

Characterization

The purity of the phases in the synthesized samples was confirmed by XRD using a Rigaku MiniFlex600 diffractometer (monochromatic radiation: Cu Kα). Scanning electron microscopy (SEM) observations combined with energy-dispersive X-ray spectroscopy (EDS) measurements were conducted on a JEOL JSM-IT100 equipped with a KEYENCE VE-9800 apparatus.

Preparation of $Pb_3Fe_2O_5F_2$ and $PbFeO_2F$ electrodes

A $Pb_3Fe_2O_5F_2$/FTO electrode was prepared by performing electrophoretic deposition in 50 mL of acetone (>99.5%, Kanto Chemical) containing ca. 100 mg $Pb_3Fe_2O_5F_2$ powder and ca. 20 mg iodine (>99.8%, FUJIFILM Wako Pure Chemical).[3] Two fluorine-doped tin oxide (FTO) substrates in parallel were immersed in the solution with a separation of ca. 15 mm, and then a voltage of 30 V was applied between the substrates for 2 minutes using a stabilized DC power supply (PSW 80–13.5, GW Instek). The $Pb_3Fe_2O_5F_2$ deposited area was 3.8 cm^2 (ca. 1.5 cm × 2.5 cm). After that, the as-deposited $Pb_3Fe_2O_5F_2$/FTO electrode was heated at 573 K for one hour to enhance the conductivity in the electrode. A $PbFeO_2F$/FTO electrode was also prepared in the same way. The amount of particles deposited onto the FTO substrate was 4–5 mg.

Electrochemical measurements

Electrochemical measurements were performed using a potentiostat (HZ-Pro, Hokuto Denko) and an electrochemical cell at room temperature. The cell body was made of Pyrex glass, and was a three-electrode-type system equipped with a Pt wire and an Ag/AgCl electrode (saturated KCl aqueous solution) as the counter and reference electrodes, respectively. 0.1 M aqueous K_3PO_4 (>98.0%, Sigma-Aldrich) solution served as the electrolyte, which was saturated with argon gas prior to undertaking measurements. The potentials measured by the Ag/AgCl reference electrode were converted to those with respect to the reversible hydrogen electrode (RHE, $E_{\mathrm{RHE}} = E_{\mathrm{Ag/AgCl}} + 0.059\ \mathrm{pH} + 0.197$ at 298 K). In this work, the electrocatalytic activities were reported based on the use of current densities per geometric area of electrode (μA $cm^{-2}{}_{geo}$).

Electrochemical impedance spectroscopy measurement was conducted using the same potentiostat and electrochemical setup. This measurement conditions were set to an AC amplitude of 10 mV and a frequency range of 100 kHz to 0.1 Hz.

Quantification of electrochemical O_2 evolution

Quantification of the O_2 evolved during controlled-potential electrolysis was performed with a gastight H-type electrochemical cell that had two chambers parted by a perfluorinated membrane (Nafion 117, Sigma-Aldrich). The $Pb_3Fe_2O_5F_2$/FTO working and the Ag/AgCl reference electrode were separated from a Pt wire counter electrode in each chamber. The cell operating conditions were identical to those in the above description of the electrochemical measurements. The evolved O_2 was detected using a gas chromatograph (MGC3000A, Inficon) equipped with a thermal conductivity detector and an MS-5A column. Argon gas was used as the carrier gas in the gas chromatograph.

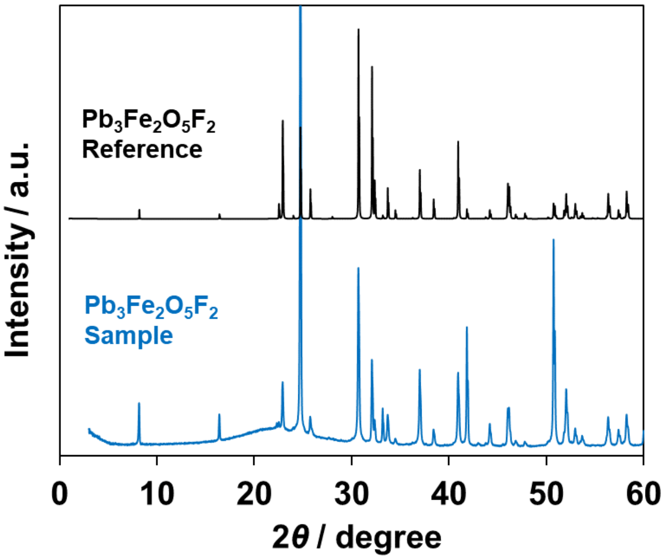

Fig. S1. XRD patterns for the synthesized $Pb_3Fe_2O_5F_2$ and the reference. The pattern for the reference was drawn based on published crystallographic data.[1]

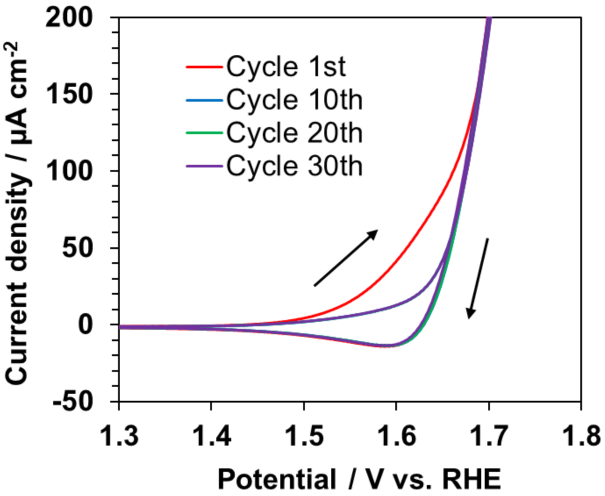

Fig. S2. Current–potential curves in each cycle for the $Pb_3Fe_2O_5F_2$/FTO electrode in aqueous 0.1 M K_3PO_4 solution (pH 12.6), as recorded at a sweep rate of 10 mV s^{-1}. After the 10th scan, no change in the CV profile was observed, indicating that this electrode was sufficiently stable for water oxidation. The oxidation wave observed at +1.6–1.7 V vs. RHE in the 1st scan might show the oxidation of Fe and/or Pb species in the $Pb_3Fe_2O_5F_2$, as already mentioned in the main text.

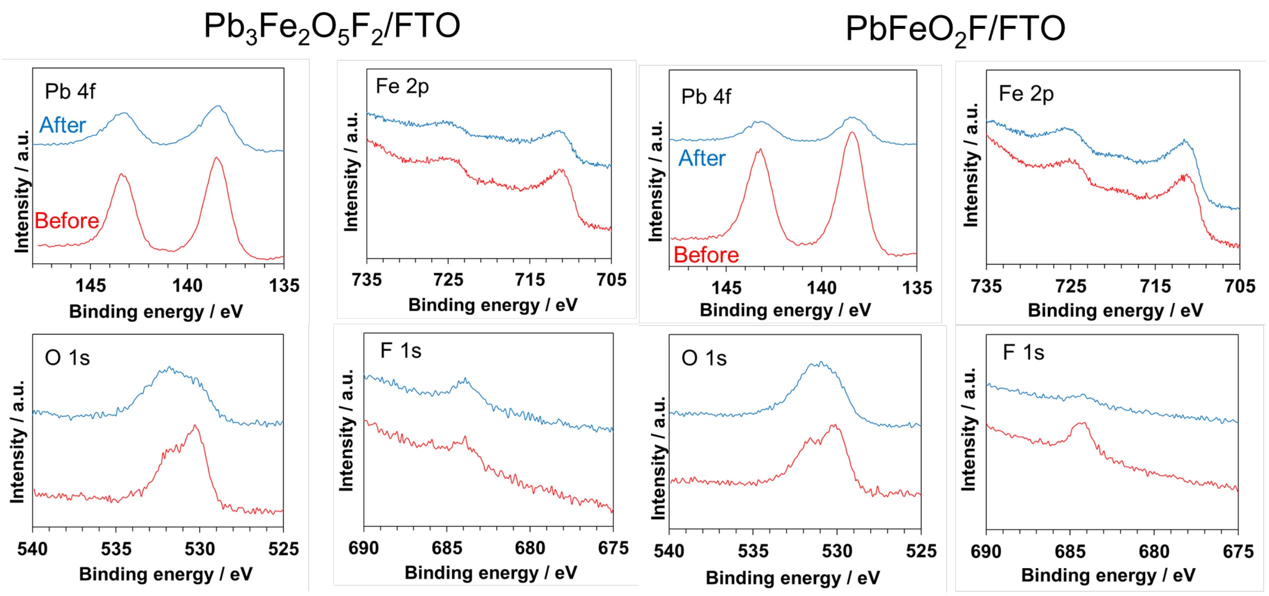

Fig. S3. Pb 4f, Fe 2p, O 1s and F 1s XPS data for the $Pb_3Fe_2O_5F_2$ and $PbFeO_2F$ electrodes before (red) and after (blue) the controlled-potential electrolysis (Fig. 5).

Table S1. Surface atomic ratios of the $Pb_3Fe_2O_5F_2$ and $PbFeO_2F$ electrodes before and after the controlled-potential electrolysis (Fig. 5)

Entry	Electrode	Surface atomic ratios[a]	
		Pb/Fe	F/Fe
1	$Pb_3Fe_2O_5F_2$ (before)	0.61	0.11
2	$Pb_3Fe_2O_5F_2$ (after)	0.51	0.14
3	$PbFeO_2F$ (before)	0.73	0.20
4	$PbFeO_2F$ (after)	0.15	0.06

[a] Determined by the corresponding XPS peak area.

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