Supplementary Information

Methods

Powder synthesis

All of the eight polycrystalline iridates except the three pyrochlore phases were synthesized by a conventional solid-state reaction via a mixed oxide technique. CaCO₃ (99.995%, Sigma-Aldrich), SrCO₃ (>99.9%, Sigma-Aldrich), BaCO₃ (99.999%, Sigma-Aldrich), and IrO₂ (99.99%, Alfa Aesar) were starting materials for the synthesis of all the Ca-, Sr-, and Ba-based iridates. Powder mixtures of the starting materials with a slight excess of Ir for the iridates were ball-milled in high-purity ethyl alcohol for 24 h. The dried slurries were then calcined at 1000–1300°C in air for 5–12 h to finally obtain polycrystalline particles. Specific synthesis conditions are as follows. a) $CaCO_3$: $IrO_2 = 1 : 1.2$ with calcination at 1000°C for 10 h followed by re-calcination at 1000°C for 10 h after grinding for CaIrO₃; b) CaCO₃ : $IrO_2 = 2 : 1.2$ with calcination at 1000°C for 10 h followed by re-calcination at 1050°C for 10 h after grinding for Ca_2IrO_4 ; c) $CaCO_3$: $IrO_2 = 4$: 1.15 with calcination at 1200°C for 10 h for Ca_4IrO_6 ; d) $SrCO_3$: $IrO_2 = 1$: 1 with calcination at 1000°C for 10 h for SrIrO₃; e) SrCO₃: $IrO_2 = 2$: 1.1 with calcination at 1100°C for 10 h for Sr₂IrO₄; f) SrCO₃ : IrO₂ = 4 : 1.1 with calcination at 1200°C for 30 min followed by re-calcination at 1300°C for 5 h after grinding for Sr₄IrO₆; g) BaCO₃ : $IrO_2 = 1 : 1$ with calcination at 1000°C for 10 h for BaIrO₃; h) BaCO₃ : $IrO_2 = 4 : 3.1$ with calcination at 1050°C for 10 h for Ba4Ir3O10. A sol-gel process was used to synthesize the pyrochlore-type iridates. Y(NO₃)₃·6H₂O (99.8%, Sigma-Aldrich) and IrCl₃·3H₂O (53~56% of Ir, Acros Organics) for a Y₂Ir₂O₇ phase and Pr(NO₃)₃·6H₂O (99.9%, Sigma-Aldrich), Nd(NO₃)₃·6H₂O (99.9%, Sigma-Aldrich), and IrCl₄ (99.95%, Alfa Aesar) for the other two pyrochlore phases, Pr₂Ir₂O₇ and Nd₂Ir₂O₇, were utilized during the process. The following stoichiometric amounts of the starting materials were first dissolved in deionized water with an addition of citric acid (>99.5%, Sigma-Aldrich) as an chelating agent to obtain transparent solutions. Each of these solutions was evaporated at 100°C to acquire a gel-type precursor and was followed by annealing at 400°C for 2 h. These precursor powders were finally calcined at 1050°C for 12 h for all the three pyrochlore-type iridates to obtain polycryalline particles. The initial stoichiometry information is as follows. a) $Y(NO_3)_3 \cdot 6H_2O$: $IrCl_3 \cdot 3H_2O = 1$: 1 for $Y_2Ir_2O_7$; b) $Pr(NO_3)_3 \cdot 6H_2O$: $IrCl_4 = 1 : 1.1$ for $Pr_2Ir_2O_7$; c) $Nd(NO_3)_3 \cdot 6H_2O$: $IrCl_4 = 1 : 1.1$ for Nd₂Ir₂O₇. Commercially available rutile-type IrO₂ nanoparticles (99.9%, Sigma-Aldrich) were used as a reference. The single-phase crystallinity of synthesized powders was confirmed by X-ray diffractometry (X'Pert-PRO MRD, PANalytical and SmartLab, Rigaku) with $Cu-K_{\alpha}$ radiation.

Electrochemical measurements

All electrochemical measurements were carried out with a potentiostat (Biologic SP-300) in a 0.5 M H₂SO₄ aqueous electrolyte solution (pH ~0.4) prepared by using the Milli-Q water (18.2 M Ω ·cm) and H₂SO₄ solution (99.999%, Sigma-Aldrich). A Pt counter electrode and a saturated

Ag/AgCl reference electrode were used for the measurements. The measured potential values *vs*. the Ag/AgCl reference electrode were converted into the RHE scale by using the following equation at 25°C,

$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \cdot \text{pH} + E^{\circ}_{\text{Ag/AgCl}}$

where $E_{\rm RHE}$ is the converted potential vs. RHE, $E_{\rm Ag/AgCl}$ is the measured potential against the Ag/AgCl reference electrode, and $E^{\circ}_{Ag/AgCl}$ is the standard potential of Ag/AgCl (KCl 3M) at 25°C, *i.e.* 0.21 V. Each of the test inks was prepared for particle-type samples by using K⁺exchanged 5-wt% Nafion solution (Nafion 117, Sigma-Aldrich, 350 µL) as binder, acetylene black (Alfa Aesar, 3.5 mg), and catalyst oxide particles (35 mg) along with high-purity ethyl alcohol (4.65 mL). The adequate amount of the ink was drop-cast on the glassy carbon of a rotating ring disk electrode (3 mm in diameter, RRDE-3A, ALS) so that the amount of catalysts loaded on the electrode was adjusted to be $0.5 \text{ mg cm}^{-2}_{\text{disk}}$. The rotating disk electrode was kept a rotation speed of 2400 rpm for all the measurements. All electrolyte solutions were presaturated by bubbling O₂ for 30 min under constant O₂ bubbling. Cyclic potential was applied to the samples at a rate of 10 mV/sec, sweeping from 1.1 up to 1.65 V (or 1.76 V in some cases) vs. RHE for the OER current measurements. Electrochemical impedance spectroscopy was also carried out in the same potentiostat in a frequency range from 0.1 Hz to 1 MHz with an amplitude of 10 mV for *i*R correction of the uncompensated series resistance (R). To track the variation of the electrochemical active surface area with anodic cycling, the double-layer capacitance was measured in a non-faradaic potential range (0.95–1.20 V vs. RHE) by recording the current values as a function of scan rate. To consider the contribution of the acetylene black to the overall double-layer capacitance of the particle-based samples, the capacitance without oxide catalysts was also measured in an identical manner with cycling. Its contribution was verified to be marginal (less than 5%) at each number of cycles. All the specific current values in the unit of A g^{-1} in this work are based on the normalization to the initial oxide mass. The chemical analysis by inductively coupled plasma – optical emission spectrometry (ICP-OES720, Agilent) was performed to determine the relative amount of Ba, Sr, and Ir dissolved into the electrolyte solutions after the anodic cycling test.

SEM, STEM, EDS, EELS, and XPS

The polycrystalline microstructure of powder samples was examined in a scanning electron microscope (SU5000, Hitachi) at 15 kV. For STEM observation of particles, each of the samples was ultrasonically dispersed in high-purity ethyl alcohol for 10 min and several drops were taken on a lacey-carbon-film Cu grid and subsequently dried in an oven at 60°C for 1 h. STEM images were taken with a transmission electron microscope (Titan cubed G2 60-300, Thermo Fisher Scientific) at 200 kV with a spherical aberration corrector (CEOS GmbH). The optimum size of the electron probe was ~1 Å with a convergence semiangle of 23 mrad. The collection semiangles of the HAADF detectors were set to 79.5–200 mrad. The obtained raw images were band-pass filtered to reduce background noise. EDS mapping of polycrystalline particles was performed in another transmission electron microscope (Talos F200X, Thermo Fisher Scientific) at 200 kV along with four integrated silicon-drift EDS detectors (ChemiSTEMTM technology) at a high beam-current rate of 1.6 nA cm⁻² for efficient and rapid

acquisition of X-ray signals. Ca- K_{α} (3.7 keV), Sr- K_{α} (14.2 keV), Ba- L_{α} (4.5 keV), Y- K_{α} (15.0 keV), Pr- L_{α} (5.0 keV), and Ir- L_{α} (9.2 keV) lines were selected during elemental mapping. The EDS maps were low-pass filtered using Bruker ESPRIT software after the reduction of background noise for better visualization. EELS analysis was conducted with a Gatan Image Filter (GIF Quantum 965, Gatan Inc.) in the Titan cubed G2. Electron energy-loss spectra for the Ca- $L_{2,3}$, Ba- $M_{4,5}$ O-K edges were acquired for spectrum imaging with a dispersion of 0.25 eV per channel and a collection aperture of 5 mm in diameter. X-ray photoelectron spectroscopy was carried out in a spectroscope (K-Alpha XPS, Thermo Scientific) with monochromatic Al-K α radiation and flood gun emission of 150 μ A in order to examine whether the Ir $4f_{5/2}$ and $4f_{7/2}$ peaks shift after anodic cycling.

DFT calculations for DOS

Ab initio DFT calculations for DOS of the iridates were carried out within the spin-polarized generalized-gradient approximation (GGA) along with the PBEsol functional revised for exchange correlation of densely packed solids and the ultrasoft pseudopotentials for ionic cores, as implemented in the CASTEP code (Biovia Inc.). High-spin $(t_{2g}^3)(e_g^2)$ for a $5d^5$ Ir⁴⁺ configuration was assumed in all the iridates for simplicity. The plane-wave basis set for the kinetic energy cutoff was 500 eV. Relaxation of the internal coordinates in the unit cell performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm with convergence tolerances of 0.1 eV Å⁻¹ for the maximum ionic force, 5×10^{-5} eV/atom for the total energy, and 0.005 Å for the maximum ionic displacement.

Supplementary Movies

- Movie S1. 3D visualization of the BaIrO₃ structure (Group A)
- Movie S2. 3D visualization of the Ca₂IrO₄ structure (Group A)
- Movie S3. 3D visualization of the SrIrO₃ structure (Group B)
- Movie S4. 3D visualization of the CaIrO₃ structure (Group B)
- Movie S5. 3D visualization of the $A'_2Ir_2O_7$ (A' = Y, Pr, Nd) structure (Group B)
- Movie S6. 3D visualization of the Ba₄Ir₃O₁₀ structure (Group C)
- **Movie S7.** 3D visualization of the Sr₂IrO₄ structure (Group C)
- **Movie S8.** 3D visualization of the Car₄IrO₆ structure (Group C)

BET Current density surface Catalyst Electrolyte Reference (mA/cm^{2}_{oxide}) area @ 1.58 V vs. RHE (m^2/g) Ba₂NdIrO₆ N/A 7 0.1 M HClO_4 **S**1 Ba₂PrIrO₆ N/A 5 0.1 M HClO_4 **S**1 $SrCo_{0.9}Ir_{0.1}O_{3-\delta}$ 0.175 30 0.1 M HClO_4 S2 0.9 0.1 M HClO₄ 3.2 S3 SrIrO₃ (@1.55 V vs. RHE) 6.1 Sr_2IrO_4 2.8 0.1 M HClO_4 S3 (@1.55 V vs. RHE) 0.7 Sr_4IrO_6 12 0.1 M HClO₄ S3 (@1.55 V vs. RHE) N/A $10 (mA/cm_{geo}^2)$ 0.1 M HClO_4 S4 Ca_2IrO_4 $Bi_2Ir_2O_7$ 46 $6 (mA/cm^2_{geo})$ $1 \text{ M H}_2 \text{SO}_4$ S5 0.08 $Y_2Ir_2O_7$ 0.1 M HClO_4 **S6** 21 (@1.525 V vs. RHE) $Y_2Ir_2O_7$ 7.3 2 0.1 M HClO_{4} **S**7 5 $Nd_2Ir_2O_7$ 1.53 0.1 M HClO_4 **S**8 (@1.53 V vs. RHE) 13 $Pr_2Ir_2O_7$ 1.55 0.1 M HClO_4 **S**8 (@1.53 V vs. RHE)

Table S1. Summary of OER current densities of iridates in previous reports

S1. O. Diaz-Morales, S. Raaijman, R. Kortlever, P. J. Kooyman, T. Wezendonk, J. Gascon, W. T. Fu and M. T. Koper, *Nat. Commun.*, 2016, **7**, 12363.

S2. Y. Chen, H. Li, J. Wang, Y. Du, S. Xi, Y. Sun, M. Sherburne, J. W. Ager III, A. C. Fisher and Z. J. Xu, *Nat. Commun.*, 2019, **10**, 572.

S3. A. L. Strickler, D. Higgins and T. F. Jaramillo, ACS Appl. Energy Mater., 2019, 2, 5490–5498.

S4. Y. Wu, W. Sun, Z. Zhou, W. Q. Zaman, M. Tariq, L. Cao, and J. Yang, *ACS Omega*, 2018, **3**, 2901–2908.

S5. K. Sardar, S. C. Ball, J. D. B. Sharman, D. Thompsett, J. M. Fisher, R. A. P. Smith, P. K. Biswas, M. R. Lees, R. J. Kashtiban, J. Sloan, and R. I. Walton, *Chem. Mater.*, 2012, 24, 4192–4200.

S6. D. Lebedev, M. Povia, K. Waltar, P. M. Abdala, I. E. Castelli, E. Fabbri, M. V. Blanco, A. Fedorov, C. Copéret, N. Marzari and T. J. Schmidt, *Chem. Mater.*, 2017, **29**, 5182–5191.

S7. P.-C. Shih, J. Kim, C.-J. Sun, and H. Yang, *ACS Appl. Energy Mater.*, 2018, 1, 3992–3998.
S8. C. Shang, C. Cao, D. Yu, Y. Yan, Y. Lin, H. Li, T. Zheng, X. Yan, W. Yu, S. Zhou and J. Zeng, *Adv. Mater.*, 2019, 31, 1805104.



Figure S1. Powder X-ray diffraction results for phase verification. In addition to the reference IrO_2 sample, three Ca-based iridate powders (CaIrO₃, Ca₂IrO₄, and Ca₄IrO₆) are confirmed to be successfully synthesized, although a very small amount of impurity phases is included in some cases.



Figure S2. Powder X-ray diffraction results for phase verification. Three Sr-based iridate powders (SrIrO₃, Sr₂IrO₄, and Sr₄IrO₆) and a BaIrO₃ powder are confirmed to be successfully synthesized, although a very small amount of impurity phases is included in Sr₄IrO₆.



Figure S3. Powder X-ray diffraction results for phase verification. A $Ba_4Ir_3O_{10}$ powder and three pyrochlore-phase iridate powders ($Y_2Ir_2O_7$, $Pr_2Ir_2O_7$, and $Nd_2Ir_2O_7$) are confirmed to be successfully synthesized, although a very small amount of Ir and IrO_2 impurity phases is included in the pyrochlore iridates.



Figure S4. Series of SEM images of the powder samples showing the particle morphologies. In contrast to the reference IrO_2 nanoparticles, the size of many synthesized iridate samples is at the micron level. A specific value of the BET surface area is also provided in yellow in each of the images.



Figure S5. Cyclic voltammograms and charging currents for DL capacitance measurements in powder samples. Two sets of results for (**a**) BaIrO₃ and (**b**) Ca₂IrO₄ are exemplified. Cyclic voltammograms were acquired in a non-faradaic region at different scan rates. The double-layer anodic charging currents are plotted as a function of the scan rate in each case. A notable increment of the double-layer capacitance up to more than 1000 μ F at the 150th cycle is demonstrated in both iridates.

BalrO₃ (Group A)



Figure S6. Additional EDS composition maps of $BaIrO_3$ (Group A). Sets of EDS maps are provided to show the formation of a Ba-deficient and Ir-rich surface layer due to Ba leaching. With anodic cycling, the thickness of the surface layer increases, as can be observed in the 100-cycle maps.

Ca₂IrO₄ (Group A)



Figure S7. Additional EDS composition maps of Ca_2IrO_4 (Group A). Sets of EDS maps are provided to show the formation of a Ca-deficient and Ir-rich surface layer due to Ca leaching. With anodic cycling, the thickness of the surface layer increases, as can be observed in the 100-cycle maps.



Figure S8. X-ray powder diffraction results of Group-A iridates. Neither variation of the Braggreflection position nor appearance of additional peaks is found after 100 anodic cycles in (**a**) $BaIrO_3$ and (**b**) Ca_2IrO_4 .



Figure S9. EELS analysis results of the Group-A iridates. The variations of the O *K*-edge in addition to the Ca *L*-edge and the Ba *M*-edge in a nanoscale interval from the surface were examined in (**a**) Ca₂IrO₄ and (**b**) BaIrO₃ during the EELS analysis. In good agreement with the EDS maps, the amorphous surface layers are Ca- and Ba-deficient in Ca₂IrO₄ and BaIrO₃, respectively, showing substantial intensity reduction of the Ca *L*- and Ba *M*-edges. The major peaks in the O *K*-edge are associated with the hybridization of the O 2*p* orbitals with the Ir 5*d* t_{2g} and e_g orbitals. In this regard, unless the coordination geometry between Ir and O remarkably changes in the structure, the position of the major peaks in the O *K*-edge would not significantly vary. As indicated by vertical lines in the O *K*-edge in Ca₂IrO₄, the position of the two major peaks denoted by 1 (O 2*p* and Ir 5*d* t_{2g} hybridization) and 2 (O 2*p* and Ir 5*d* e_g hybridization) is identified to be nearly unchanged in the Ca-deficient surface layer. This strongly supports that the basic [IrO₆] framework is preserved despite Ca leaching. Similar intensity reduction of the Ba *M*-edge is consistently observed in the surface layer of BaIrO₃. In addition, although broadening of peaks 1 and 2 in the O *K*-edge plot is shown, their position does not appear to be seriously vary.



Figure S10. Atomic-column-resolved HAADF images for the amorphous surface layers. Even though the amorphization is induced by Ba and Ca leaching at the surface, the basic connectivity between the $[IrO_6]$ is observed not to completely collapse, showing the local short-range order, as indicated by arrows in the magnified images for Ca₂IrO₄ and BaIrO₃.



Figure S11. Additional HAADF-STEM images of the iridates in Groups A and B. In addition to the amorphous nature of the surface layers, the rough surface characteristics can be verified in accordance with the large DL capacitance values. (a) During the STEM observation, it was found that the thickness of the amorphous surface layers after 30 cycles is more than 2 nm on average in the Group-A iridates. (b) In contrast, most surface layers in SrIrO₃ and CaIrO₃ in Group B after 30 cycles were fairly thin, showing more or less 1 nm, as exemplified in the images.



Figure S12. X-ray photoemission spectroscopy (XPS). Rutile-type IrO_2 was taken as a reference crystal having Ir^{4+} for easier comparison of the chemical shift before and after anodic cycling. As shown below, the valence state of Ir was identified to become higher after 100 cycles in all the four iridtes, demonstrating that both Ir $4f_{5/2}$ (65 eV) and $4f_{7/2}$ (62 eV) peaks shift toward higher energy values (see red broken lines in each spectrum after 100 cycles). This chemical shifts thus indicate that a substantial amount of Ir in the amorphous surface layers after alkaline-earth leaching is in the state of a higher than 4+.

Ba₄Ir₃O₁₀ (Group C)



Figure S13. Additional EDS composition maps of $Ba_4Ir_3O_{10}$ (Group C). Sets of EDS maps are provided to show substantial Ba leach-out even after 30 cycles. With further anodic cycling, locations with the Ba-deficient and Ir-rich composition are more frequently observable.

Sr₂IrO₄ (Group C)



Figure S14. Additional EDS composition maps of Sr_2IrO_4 (Group C). Sets of EDS maps are provided to show the substantial Sr leach-out even after 10 cycles. No detectable Sr after 100 cycles is noted, directly indicating nearly complete Sr leaching from a Sr_2IrO_4 particle. The numeric information on the Ir maps denotes the two-dimensional area of each particle. The noticeable reduction of the particle size after 100 cycles indicates significant dissolution of [IrO₆] octahedral units and subsequent lattice collapse.

Ca₄IrO₆ (Group C)



Figure S15. Additional EDS composition maps of Ca_4IrO_6 (Group C). Sets of EDS maps are provided to show the substantial Ca leach-out even after 30 cycles. No detectable Ca after 100 cycles in the particles is noted, directly indicating nearly complete Ca leaching. The numeric information on the Ir maps denotes the two-dimensional area of each particle. The remarkable reduction of the particle size after 100 cycles indicates significant dissolution of [IrO₆] octahedral units and subsequent lattice collapse.

Sr₄IrO₆ (Group C)



Figure S16. Additional EDS composition maps of Sr_4IrO_6 (Group C). Sets of EDS maps are provided to show the substantial Sr leach-out. No detectable Sr after 100 cycles in the particles is noted, directly indicating nearly complete Sr leaching. The numeric information on the Ir maps denotes the two-dimensional area of each particle. The remarkable reduction of the particle size after 100 cycles indicates significant dissolution of [IrO₆] octahedral units and subsequent lattice collapse.



Figure S17. ICP-OES elemental analyses of electrolyte solutions. The concentration of Ba, Sr, and Ir in the electrolyte solutions after OER current measurements was quantitatively determined by using ICP-OES. (**a**) In addition to the higher dissolution concentration of Sr in the SrIrO₃-tested electrolyte than Ba in the BaIrO₃-tested electrolyte, a higher Ir concentration in the case of SrIrO₃ consistently agrees with the structurally weaker connectivity between [IrO₆] octahedra in SrIrO₃ (Group B) than BaIrO₃ (Group A). (**b**) Three Sr-based iridates are compared. Note that the dissolution of both Sr and Ir is the most serious in Sr₄IrO₆, where the [IrO₆] octahedra are completely isolated with each other with no connection. Furthermore, as the BET surface area of Sr₂IrO₄ (0.42 m² g⁻¹) and Sr₄IrO₆ (0.36 m² g⁻¹) is respectively much lower than that of SrIrO₃ (1.41 m² g⁻¹), the difference in real dissolution of Sr and Ir per unit area would be much larger between the three samples.

SrIrO₃ (Group B)



Figure S18. Additional EDS composition maps of $SrIrO_3$ (Group B). Sets of EDS maps are provided to show the formation of a Sr-deficient and Ir-rich surface layer at the nanoscale due to Sr leaching. Compared with the surface layers in the Group-A iridates, the thickness of the surface layers in SrIrO₃ does not remarkably vary with anodic cycling.

CalrO₃ (Group B)



Figure S19. Additional EDS composition maps of $CaIrO_3$ (Group B). Sets of EDS maps are provided to show the formation of a Ca-deficient and Ir-rich surface layer at the nanoscale due to Ca leaching. The magnified map in the 100-cycle-set clarifies the presence of an Ir-rich surface layer. However, the thickness of the surface layers in CaIrO₃ does not remarkably vary with anodic cycling.

Y₂Ir₂O₇ (Group B) pyrochlore phase



Figure S20. Additional EDS composition maps of $Y_2Ir_2O_7$ (Group B). Based on these sets of EDS maps, Y does not appear to seriously leach out during the OER even after 100 cycles. Although some irregular morphologies were found during the STEM observation, no significant leaching of Y was identified.

Nd₂Ir₂O₇(Group B) pyrochlore phase



Figure S21. Additional EDS composition maps of $Nd_2Ir_2O_7$ (Group B). As in the case of $Y_2Ir_2O_7$, Nd does not show any serious leach-out during the OER even after 100 cycles. Consequently, the invariant DL capacitance with cycling shown in Figure 4 in the main text appears to be consistently associated with this stability against leaching.



Figure S22. Series of DOS plots of all the eleven iridates. As indicated by red arrows, substantial densities of the O 2*p* states and the Ir 5*d* states are present near the fermi level ($E_F = 0 \text{ eV}$) and also overlap with each other. As a result, easy charge transfer between O and Ir during the OER is anticipated, consistently supporting their high OER activities, as shown in Figure 1 in the main text. Note that a high-spin Ir⁴⁺ 5*d*⁵ configuration is assumed during the DFT caclautaions for simplicity.



Figure S23. OER activity and DL capacitance measurements of the reference IrO_2 sample. In contrast to the Group-A iridates, IrO_2 shows gradual decrement in both the OER specific current and the DL capacitance. Except the initial rise of the DL capacitance during 10 cycles, these variations in the OER activity and the DL capacitance resemble those observed in the pyrochlore phases in Group B. Therefore, the loss of OER activity with cycling appears to relate with the disassembly of cornershared [IrO₆] octahedra and subsequent dissolution during the OER.