Supporting Information to

**CO\textsubscript{2}-free electric power circulation via direct charge and discharge using the glycolic acid/oxalic acid redox couple**

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**METHODS**

**Materials**
Titanium tetrabutoxide (95.0%), 2-propanol (99.9%), sodium sulfate (99.0%), methanol (99.5%), sulfuric acid (95.0%), oxalic acid (\textit{OX}, 98.0%), glyoxylic acid monohydrate (GO, 95.0%) and glycolic acid (\textit{GC}, 97.0%) were purchased from Wako; N,N-dimethylformamide (99.5%) was purchased from Kanto; Al (99%), Ti (99.5%), V (99.7%), Ni (99%), Zr (99.2%), Nb (99.9%), Mo (99.95%), Cu (99.9%), Sn (99.9%), Pb (99.95%) foils were purchased from Nilaco. All chemicals were used without further purification.

**Synthesis of layered protonated titanate**
The layered protonated titanates (LPTs) were synthesised according to a previously reported procedure\textsuperscript{1}. A mixture of 1 mL of titanium tetrabutoxide, 10 mL of 2-propanol and 30 mL of \textit{N},\textit{N}-dimethylformamide were transferred into a 50 mL Teflon-lined autoclave and heated in an electric oven at 200 °C for 20 h. Finally, the product was collected by centrifugation and washed thoroughly with acetone and methanol.

**Synthesis of porous TiO\textsubscript{2} spheres**
The porous TiO\textsubscript{2} spheres (PTSs) were synthesised by calcination of LPTs under flowing air at 150, 300, 450, 500, 525, 550 or 600 °C for 1 h; the heating rate was 100 °C/h.

**Structural characterization**
TEM and HRTEM images were collected on a JEM-2010HCKM (JEOL) operated at 200 kV. An STEM observation and EELS mapping were conducted on a JEM-ARM200F (JEOL) at Kyushu University operated at 200 kV. Sample grids for the TEM, HRTEM, STEM and EELS observations were prepared by dropping ethanol dispersions of the specimens onto a copper grid with no metal coating. XRD measurements were conducted using a SmartLab (Rigaku) with Cu-K\textalpha radiation (\(\lambda = 1.54059\) Å) at 45 kV and 200 mA. Nitrogen adsorption-desorption measurements were performed at -196 °C on a BELSORP-max (Bel Japan). The Brunauer-Emmett-Teller (BET) specific surface areas were calculated from the adsorption data in the relative pressure ranging from 0.04 to 0.2\textsuperscript{2}. Pore size distributions were calculated using the isotherms based on the Barrett-Joyner-Halenda (BJH) formula\textsuperscript{3}. XPS spectra were recorded on a VersaProbeII (ULVAC-PHI) with Al anode X-ray source. Binding energies were corrected by referring a C 1s binding energy of the carbon atoms of the ligand in the specimens at 284.5 eV. The obtained XPS spectra were reproduced using a combination of Gaussian and Lorentzian functions. UV-vis spectra were recorded on a V-670 spectrometer (JASCO). The diffuse reflection spectra were converted into reflectance spectra using the Kubelka-Munk function.
Preparation of electrodes of a variety of metal and metal oxide electrodes
Al, Ti, V, Ni, Zr, Nb and Mo foils (2×2 cm) were used after calcination at 450 ºC for 0.5 h under air flow. Cu, Sn and Pb foils (2×2 cm) and a Pt coil (23 cm) were used without calcination.

Preparation of TiO$_2$ catalyst loading Ti foil electrodes
Suspensions of TiO$_2$ catalyst (10 or 20 mg) in methanol (0.2 mL) were applied to Ti foils (2 × 2 cm$^2$) previously processed at 450 ºC for 0.5 h. The TiO$_2$-catalyst-mounted Ti foils were calcined at 150, 300, 450, 500, 525, 550 and 600 ºC under flowing air.

Electrochemical measurements
All electrochemical experiments were conducted using a three-electrode system connected to a VersaSTAT4 potentiostat (AMETEC, Princeton Applied Research). A coiled Pt wire (230 × 0.5 mm$^2$, BAS) was used as a counter electrode. An Ag/AgCl (RE-1B, BAS) or an Hg/HgO (RE-6A, BAS) reference electrode was used in acidic or alkaline conditions, respectively. Potentials applied to the working electrode were measured against a reference electrode and converted to the RHE reference scale using:

\[ E \text{ (versus RHE)} = E \text{ (versus Ag/AgCl)} + 0.199 V + 0.059 V \times \text{pH} \]
\[ E \text{ (versus RHE)} = E \text{ (versus Hg/HgO)} + 0.110 V + 0.059 V \times \text{pH} \]

OX electrochemical reduction at a constant potential (chronoamperometry, CA) and product analysis
The electrochemical reduction of OX at a constant potential, i.e., chronoamperometry (CA), was performed in a two-compartment electrochemical cell sealed with Teflon caps to be gas-tight. A piece of proton-conducting membrane (Nafion®, NRE-212, Sigma-Aldrich) was used as a separator. An aqueous electrolyte solution (40 mL of 0.16 or 0.03 M OX and 0.16 or 0.20 M Na$_2$SO$_4$) was introduced into a cathodic cell (75 mL in volume), and working, reference, and counter electrodes were placed inside the cell. The pH value of the electrolyte solution (40 mL of 0.16 or 0.20 M Na$_2$SO$_4$) in the anodic cell was adjusted by the addition of H$_2$SO$_4$ to be identical to that of the electrolyte solution in the cathodic cell. After the Teflon caps were tightly closed, Ar gas was bubbled into both the cathodic and anodic cells for 30 min to purge the air from the cells. OX electrochemical reductions were conducted by controlling the working electrode potential using a VersaSTAT4 potentiostat. The reaction solution (50 µL) was collected from the cathodic cell and analysed using a high-performance liquid chromatograph (HPLC, LC-20AD, Shimadzu) equipped with a refractive-index detector (RID-10A, Shimadzu) and a diode-array detector (SPD-M20A, Shimadzu).

GC electrochemical oxidation and product analysis
An ethylene glycol (0.9 g) suspension of 20 wt.% Pt/C (50.5 mg, Wako) was applied onto carbon felts (4 cm$^2$ × 4 felts, 16 cm$^2$ total). The loaded felts were heat-treated under N$_2$ gas at 400 ºC for 30 min and then under H$_2$ gas at 300 ºC for 10 min. Electrooxidation reactions were performed in a two-compartment electrochemical cell sealed to be gas-tight with Teflon caps. A piece of proton-conducting membrane was used as a separator. Aqueous electrolyte solution (50 mL of 20 wt.% KOH, 0.5 M GC) was introduced into an anodic cell (75 mL in volume) into which the working and reference electrodes (Hg/HgO) were subsequently immersed. A counter electrode was placed in a cathodic cell (75 mL in volume) containing aqueous electrolyte solution (50 mL, 20 wt.% KOH). After the Teflon caps were tightly closed, N$_2$ gas was bubbled in both the anodic and cathodic cells for 30 min to purge the air from the cell. GC electrooxidation was conducted at 1.2 V and 50 ºC for 2 h, where the potential was controlled using a VersaSTAT4 potentiostat. The chemical composition of the reaction solution (50 µL) collected from the cathodic cell was analysed using HPLC.

Definition of Faraday efficiency
The Faraday efficiency in the electroreduction experiments is defined by the following equation:

\[ \text{Faraday efficiency (\%)} = \frac{m_{\text{products}} \times n \times F}{Q} \times 100, \]

where $m_{\text{products}}$ is the moles of reduction products; $n$ represents the number of electrons required for the formation of GO and GC from OX (n = 2 and 4 for the formation of GO and GC, respectively) or OX from GC (n = 4 for formation of OX); F is Faraday’s constant (96,485 C/mol of electrons); and Q is the total charge in Coulombs passed across the electrode during the electrolysis.
Cyclic voltammetry (CV) measurements
CV measurements were conducted by employing a three-electrode system connected to a VersaSTAT4 potentiostat. An electrolyte aqueous solution (80 mL of 0.03 M OX and 0.20 M Na₂SO₄) was introduced into a glass cell (100 mL in volume, ALS). After the glass cell was tightly sealed with Teflon cap, Ar gas was bubbled for 30 min in order to purge the air from the inside of the cell. The current value was recorded against the applied potential with 10 mV/s scan rate and 5 scan cycles. The CV measurement for a blank solution was carried out by following the same procedures abovementioned except for using electrolyte solution (80 mL of 0.20 M Na₂SO₄).

Alkaline fuel cell (AFC) tests
A direct glycolic acid AFC was fabricated using pelletised LaSr₃Fe₃O₁₀ powder as an electrolyte. The LaSr₃Fe₃O₁₀ powder was synthesised by a solid-state reaction using a procedure previously reported in the literature. A pressed and pelletised LaSr₃Fe₃O₁₀ disc (20 mm in diameter and 1 mm in thickness) was pretreated and used as an electrolyte. For the preparation of an anodic electrode, an ethylene glycol (EG) paste containing LaSr₃Fe₃O₁₀ and a commercial Pt catalyst (TEC10E40E, Tanaka) was shaped into a 5 mm diameter disk. The anodic and cathodic electrodes were exposed to an aqueous solution (2 M GC, 4 M KOH) at 70 ºC and under flowing, wet O₂ flow. Electromotive force and electron density were recorded at a scan rate of 11 mA/s using a potentiostat (Autolab, Metrohm) connected to the cell fixtures.

OX adsorption tests
OX adsorption experiments were performed by suspending 10 mg PTS-500 or PTS-600 in 5 mL of aqueous solution containing 22.2 mmol OX at 24 ºC for 2 h. After the adsorption, PTSs were removed from the suspension by centrifugation at 6000 rpm for 3 min. The amounts of OX adsorbed on PTSs were determined by the HPLC analysis for the supernatant solution.

Energy efficiency calculation
Energy efficiencies (η) for the OX electroreduction and GC electrooxidation on a working electrode were calculated by the following equation:

\[
\eta = \frac{V_t - |V_E|}{V_t} \times \eta_F,
\]

where \(V_t\) is a theoretical open-circuit potential using GC as a fuel, i.e., 1.1 V, \(V_E\) is an applied potential on the working electrodes, i.e., -0.6 V vs. RHE for OX electroreduction and 0.6 V vs. RHE for GC electrooxidation, and \(\eta_F\) is Faraday efficiency, i.e., 85% for OX electroreduction at -0.6 V vs. RHE and 84% for GC electrooxidation at 0.6 V vs. RHE.

Scheme S1  Comparison between hydrogen and carboxylic acid (R-COOH)/alcohol (R-OH) redox couples as energy carriers.
Product yields on Al, Ti, V, Ni, Cu, Zr, Nb, Mo, Sn and Pb in OX reductions. Al, Ti, V, Ni, Cu, Zr, Nb, Mo, Sn and Pb foils and a Pt coil were used as electrodes for OX electroreduction. Al, Ti, V, Ni, Zr, Nb and Mo foils were calcined at 450 °C. Electroreductions were performed in 0.16 M OX with 0.16 M Na₂SO₄ (pH 1.2) at -0.627 V vs. RHE at 24 °C for 2 h. Orange and blue bars represent GC and GO yields, respectively.
Scheme S2  Compounds possibly produced in the multistep reduction of OX.
Fig. S2  XRD patterns and structural properties of LPT and PTSs. (a) XRD patterns. Broken lines indicate diffraction angles of an anatase-type TiO$_2$ (JCPDF card file 01-0562). Diffraction peaks assignable to H$_2$Ti$_2$O$_5$·H$_2$O are marked with solid circles. (b) Enlarged XRD patterns in the range from 20 to 40°. The solid line indicates the diffraction angle from the (101) plane in anatase-type TiO$_2$. The diffraction peaks from the (310) plane in H$_2$Ti$_2$O$_5$·H$_2$O are marked with open circles. Baselines in the angle range from 20 to 32° are shown as broken lines. (c) I$_{A}$/I$_{A}+I_{H}$ vs. the calcination temperature, where I$_{A}$ and I$_{H}$ indicate the peak intensity from the (101) plane in anatase-type TiO$_2$ at 2θ = 25.3° and that from the (310) plane in the H$_2$Ti$_2$O$_5$·H$_2$O phase at 2θ = 27.4°, respectively. The I$_{A}$/I$_{A}+I_{H}$ values were calculated to evaluate the extent of anatase phase formation. The I$_{A}$/I$_{A}+I_{H}$ values increased with increasing calcination temperature up to 500 °C and became 1 at 500 °C, implying that PTS-500 is composed purely of the anatase phase. (d) The sizes of the crystallites formed in LTS and PTSs, as determined by Rietveld profile analysis of their XRD patterns. The calcination temperature dependence reveals that the crystallite sizes of the anatase-type TiO$_2$ domains progressively increase with increasing calcination temperature.
Fig. S3  TEM images, $N_2$ absorption isotherms and surface properties of LPT and PTSs. Low-magnification (upper) and high-magnification TEM images (lower) of PTS-300 (a and e), PTS-450 (b and f), PTS-525 (c and g), and PTS-550 (d and h). (i) Low-magnification TEM image of LPT. (j) Nitrogen adsorption-desorption isotherms of LPT and PTSs. All of the $N_2$ adsorption-desorption isotherms are classified as type IV absorption curves. Type H3 hysteresis loops were observed in the isotherms of LPT and PTS-450, suggesting that LPT and PTS-450 have slit pores arising from aggregation of the thin nanosheets. Unlike such pore structures, PTS-500, PTS-550 and PTS-600 have straight pores between the nanorods according to their isotherms without hysteresis loops. (k) BJH pore size distributions of PTS-500. The pore size distribution shows that the PTS-500 has mesopores less than 50 nm in diameter. (l) Table showing a summary of the structural properties of LPT and PTSs. Porous structures of PTSs lead to high BET surface areas and to large total pore volumes. The relatively small surface area calculated for PTS-600 is possibly attributed to the partially aggregated nanostructure, which was observed in TEM and XRD measurements.
Fig. S4  Surface properties of PTSs. (a) and (b) Ti 2p XPS spectra of PTS-500 and PTS-600, respectively. Sharp and intense Ti 2p peaks were clearly observed in the spectra of both PTSs, and the area ratios of the Ti 2p3/2 and Ti 2p1/2 peaks for PTS-500 and PTS-600 are almost identical, i.e., 0.360 and 0.340, respectively. These observations indicate that both PTSs consist only of Ti$^{4+}$ surface species. (c) and (d) O 1s XPS spectra of PTS-500 and PTS-600. (e) Table summarising OX adsorption properties of PTS-500 and PTS-600. OX adsorption experiments were conducted by suspending 10 mg of PTSs in 5 mL of aqueous solution containing 22.2 mmol of OX at 24 °C for 2 h. The amounts of OX adsorbed onto the PTSs were determined by HPLC analyses.

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<tr>
<th></th>
<th>BET surface area [m$^2$/g]</th>
<th>Adsorbed OX [μmol]</th>
<th>Number of adsorbed OX per unit area [10 mm$^2$]</th>
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<tbody>
<tr>
<td>PTS-500</td>
<td>82.1</td>
<td>1.28</td>
<td>9.4</td>
</tr>
<tr>
<td>PTS-600</td>
<td>43.2</td>
<td>0.70</td>
<td>9.7</td>
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Fig. 55 Structural and surface properties of rutile-type TiO$_2$ NPs. (a) TEM image, (b) XRD pattern (c) nitrogen adsorption-desorption isotherm, and (d) BJH pore size distributions of rutile-type TiO$_2$ NPs. Broken lines shown in (b) indicate diffraction angles of rutile-type TiO$_2$ (JCPDF card file 01-1292).
Fig. S6 UV-vis and EELS spectra of PTSs. (a) UV-vis spectra of PTS-500, PTS-550, PTS-600 and rutile NPs. (b) and (c) EELS spectra of anatase- and rutile-type TiO$_2$ phases. Ti L$_3\pi$ absorption spectra show asymmetric structures, i.e., a shoulder emerging on the high-energy-loss side in anatase and on the low-energy-loss side in rutile.
Fig. S7  Structural and surface properties of bulk anatase. (a) TEM image, (b) XRD pattern (c) nitrogen adsorption-desorption isotherm, and (d) BJH pore size distributions of bulk anatase-type TiO$_2$. Broken lines shown in (b) indicate diffraction angles of an anatase-type TiO$_2$ (JCPDF card file 01-0562).
Fig. S8 CV curves for the electroreduction of OX using (a) Ti foil and (b) Ti foil modified with PTS-450, (c) PTS-500 and (d) PTS-600. Solid and broken curves represent reduction currents measured in electrolyte solutions with and without the OX substrate, respectively. The electrochemical experiments were conducted in 0.03 M OX aqueous solution including 0.2 M Na$_2$SO$_4$ or 0.2 M Na$_2$SO$_4$ (pH 2.1) aqueous solution at 24 °C.
Additional catalytic performances of PTS-500 at various potentials. Total yields (or total charges) for formation of reduction products examined at -0.7 V vs. RHE and various temperatures (top row) and at various potentials and 50 °C (bottom row). (a) Electrolysis at -0.7 V and 24 °C. (b) Electrolysis at -0.7 V and 40 °C. (c) Electrolysis at -0.7 V and 50 °C. (d) Electrolysis at -0.4 V and 50 °C. (e) Electrolysis at -0.5 V and 50 °C. (f) Electrolysis at -0.6 V and 50 °C. GC was obtained with 99% selectivity via electrolysis at 50 °C for 6 h. All electrochemical experiments, except for the blank measurement, were conducted in 0.03 M OX aqueous solution containing 0.2 M Na₂SO₄ (pH 2.1).
Fig. S10 Faraday efficiencies for a product generation in 3 successive CA experiments for OX electroreduction using PTS-500. Each OX electroreduction was conducted in 0.03 M OX aqueous solution containing 0.2 M Na₂SO₄ (pH 2.1) at -0.7 V vs. RHE and 50 °C for 6 h. Orange and blue bars represent Faraday efficiencies for GC and GO generations, respectively.