Multiscale design for high-performance glycolic acid electro-synthesis cell: Preparation of nanoscale-IrO2-applied Ti anode and optimization of cell assembling

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ABSTRACT

Performance of a polymer electrolyte alcohol electrosynthesis cell (PEAEC) using a glycolic acid (GC)/oxalic acid (OX) redox couple was enhanced via the multiscale approach, i.e., increase of reaction rate on an anode by employing nanometer-scale (nanoscale) IrO2 catalysts and increase of selectivity for GC production via optimization of cell structures, i.e., a millimeter-scale approach. We prepared nanoscale IrO2 anode catalyst, which is mixture of IrO2 nanoparticles (d = 3.7 ± 1.8 nm) and their agglomerates (d < 200 nm). The linear sweep voltammetry measurement for water oxidation revealed that the nanoscale IrO2 catalyst deposited on a porous carbon paper reduces overpotential for water oxidation by 196 mV from that obtained with an anode composed of commercial microscale IrO2 gran. Furthermore, application of the nanoscale IrO2 catalyst on porous titanium paper not only improved durability but also doubly enhanced water oxidation performance. We examined various PEAEC architectures composed of the nanoscale IrO2 applied Ti anode. Both nanometer- and millimeter-scale approaches realized the best PEAEC performance for GC production, i.e., 59.4% of energy conversion efficiency with 97.1% of Faradaic efficiency for the GC production at 1.8 V and 98.9% of conversion for 3 M OX, which is an almost saturated aqueous solution at operating temperature of the PEAEC (60°C).

1. Introduction

Variable nature and uneven dispersion of renewable energy sources, such as solar, wind, geothermal, etc., make their efficient use difficult, therefore, energy storage via the conversion of electric power generated using renewable energies into energy storable chemicals, namely energy carriers, is highly important [1–11]. Hydrogen production via water electrolysis is the most advanced technology for the power storage into an energy carrier. The high energy conversion efficiency, i.e., 59–70%, for hydrogen production has already been realized with commercial water electrolyzer [12]. However, electrolytic hydrogen is not widely applicable anywhere in the world due to difficulties in handling for chemically active and low-volumetric-energy-density hydrogen. On the other hand, alcohols have recently attracted attention as an energy carrier, because they offer multiple advantages compared to gaseous carriers, including ease in transportation, storage and handling as well as higher volumetric energy density [13–16]. In this regard, we have demonstrated direct power storage into glycolic acid (HOOC–CH2OH, GC) as an energy carrier via electro-reduction of oxalic acid (HOOC–COOH, OX), which is a bio-deliverable divalent carboxylic acid [17–20]. In this system, CO2-free electric power generation is attainable via selective electro-oxidation of GC to form OX. Recently, we have first fabricated a flow-type polymer electrolyzer for alcohol synthesis from a carboxylic acid, which is named a polymer electrolyte alcohol electrosynthesis cell (PEAEC), and demonstrated continuous electro-reduction of OX to form GC using the PEAEC without any addition of electrolyte into the reaction solution [21]. The energy conversion efficiency for the electrochemical GC production on the PEAEC reached 49.6%, which was calculated by counting overpotential and Faradaic efficiency (FE). However, the efficiency was limited due to large overpotential for water oxidation at the anode, which was composed of commercial micro-meter-size IrO2 catalyst (IrO2-micro) and a gas-diffusion carbon paper. Thus, in this study, we demonstrate very simple method for the preparation of nano-meter size IrO2 (IrO2-nano), which is mixture of IrO2.

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nanoparticles and their agglomerates, and application of IrO2-nano on Ti anode for water oxidation reaction, which showed superior activity and durability due to favorable stability brought about by combination of IrO2-nano and Ti. The subsequent optimization of the cathode structure and cell structures realized construction of a high-performance PEAEC, which enforces advantages of solution-type energy carrier.

2. Experimental

2.1. Materials

IrO2 (IrO2-micro), H2IrCl6·nH2O, Na2SO4, NaOH and OX were purchased from FUJIFILM Wako Pure Chemical Corporation and used without further purification. Ti mesh (100 mesh) and Ti felt (WB/Ti/20/150, 150 g m⁻²) were purchased from Manabe industry co., ltd and NIKKO TECHNO, Ltd., respectively. Nafion 117 (0.007 inch thickness) and Nafion solution (5 wt%) were purchased from Sigma-Aldrich, Co. Carbon paper, SIGRACET GDL 25BC, was purchased from SGL group. Carbon felt, E-525, was purchased from KUREHA CORPORATION. Ti paper, WEBTI-K (0.025 mm thickness), was purchased from Toho Technical Service, Co., Ltd. Fuel cell evaluation systems (carbon current collector with flow channels, 4–25 cm², serpentine flow) were purchased from ElectroChem, Inc. and used for the PEAEC. Lab-designed Ti bipolar plates with flow channels (4–25 cm², serpentine flow) were used for the PEAEC.

2.2. Preparation of IrO2 nanoparticles (IrO2-nano)

IrO2-nano was prepared from H2IrCl6·nH2O as starting material according to a reported procedure [22]. Aqueous solution containing H2IrCl6·nH2O (97.0 mM, 200 mL) was stirred for 45 min. at 100 °C. Aqueous solution of NaOH (1 M, 200 mL) was added to promote the formation of Ir-hydroxide and the solution was stirred for another 45 min. at 100 °C. Afterwards, the solution was centrifuged for 15 min. and filtered. The prepared non-stoichiometric hydroxide (Ir(OH)₃) was dried for 5 h at 80 °C and calcined in air at 400 °C for 1 h to obtain IrO2 powder.

2.3. Preparation of electrodes

As a cathode for electro-reduction of OX, Ti mesh and Ti felt covered with anatase-TiO2 layer (TiO2/Ti-M and TiO2/Ti-F, respectively, area: 4–25 cm²) were prepared from Ti mesh and Ti felt, respectively, through a two-step hydrothermal reaction as we reported previously [21]. IrO2-nano (Ir-micro) deposited carbon and Ti paper (IrO2-micro/C (IrO2-micro/C) and IrO2-nano/Ti, respectively) were prepared by the hand painting method [23,24] with a gas-diffusion paper (SIGRACET GDL 25BC) and a gas-diffusion Ti paper (WEBTI-K), respectively. Catalyst ink was typically prepared with sonication of 4 mg of IrO2 powder, 24 μL of Nafion solution (5 wt%), 240 μL of 2-propanol and 240 μL of water. The ink was then painted on the gas-diffusion carbon paper having area of 4 cm² (IrO2: 1 mg cm⁻²) and naturally dried in the atmosphere.

2.4. Characterisation of anode catalysts

Transmission electron microscope (TEM) images were taken on a JEM-2100 (JEOL Ltd.) at an accelerating voltage of 200 keV to examine morphology of catalyst particles.

X-ray absorption near-edge structure (XANES) spectra were recorded in the transmission mode for spectra of Ir LIII-edge at a BL 06 at the SAGA-LS (Saga, Japan) with the storage ring operating at energy of 1.4 GeV. The energy range of this light source (bending magnet) is 2.1–23 keV. A silicon (111) double-crystal monochromator was used to obtain the incident X-ray beam. The typical photon flux is 10¹⁰ photons per second. The intensities of the fluorescence X-rays were monitored with silicon drift detector. Powder of Ir-micro or Ir-micro was diluted with boron nitride to adjust to optimum concentration and then pressed into a tablet with a diameter of 1 cm. Data processing was carried out with Athena and Artemis included in the IFEFFIT package [23].

Liner sweep voltammetry (LSV) on a catalyst was conducted using a three-electrode system connected to a VersaSTAT 4 potentiostat (Princeton Applied Research). IrO2-nano/C, IrO2-micro/C, IrO2-nano/Ti or IrO2-micro/Ti, was used as a working electrode. A coiled Pt wire (length 230 mm, diameter 0.5 mm, BAS Inc.) and an Ag/AgCl (RE-1B, BAS Inc.) electrode were used as a counter electrode and a reference electrode, respectively. Potentials applied to the working electrode were measured against a reference electrode and converted to the reversible hydrogen electrode (RHE) reference scale using:

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

(1)

A typical procedure for LSV measurement is as follows. An aqueous solution containing 0.2 M Na2SO4 (pH = 6.4, 40 mL) was introduced into a glass cell (100 mL in volume) in which the working, counter and reference electrodes were subsequently immersed. After the glass cell was tightly sealed with Teflon cap, Ar gas was bubbled for 30 min. to purge the air from the inside of the cell. The current value was recorded against the applied potential with 10 mV s⁻¹ scan rate.

2.5. Preparation of membrane electrode assembly (MEA)

A MEA was prepared by a hot press method. The prepared TiO2/Ti-M, Naion 117 membrane and IrO2-nano/Ti (or IrO2-micro/C) were pressed using a hot press machine (H400-15, AS ONE Corporation) and kept at 120 °C for 4 min. After cooling to room temperature, the MEA was extracted from the press machine.

The other MEA prepared using airbrush technique [24,25] was applied to the PEAEC during the optimization of the cathode structure (Section 3.3) and the efforts for maximizing conversion of OX (Section 3.4). A Naion 117 membrane was covered with a mask (2 cm × 2 cm). The catalyst ink containing 4 mg of IrO2 powder, 24 μL of Nafion solution (5 wt%), 240 μL of 2-propanol and 240 μL of water was dispersed on the Naion 117 membrane (IrO2: 1 mg cm⁻²) using an airbrush and naturally dried in the atmosphere. The prepared TiO2/Ti-M or TiO2/Ti-F, the Naion 117 membrane having the IrO2 layer and Ti paper were pressed and kept at 120 °C for 4 min. After cooling to room temperature, the MEA was removed from the pressing machine.

2.6. Fabrication of the PEAEC

Fig. 1a illustrates a schematic view of the PEAEC equipped with MEA composed of TiO2/Ti-M, Naion membrane and IrO2 anode, i.e., IrO2-micro/C, IrO2-nano/C or IrO2-nano/Ti, between two current collectors having sample flow channels. Carbon and titanium blocks having serpentine flow patterns were utilized as current collectors (reaction area is 4–5 cm²). The prepared MEA was placed between current collectors. Silicon rubber was used as a gasket. Calcined Ti mesh and carbon felt, which are omitted in Fig. 1a for simplicity, were also inserted behind the MEA on the cathode and anode sides, respectively, to make a better electrical contact with the carbon current collectors. To construct PEAEC with Ti current collectors, Ti felt was inserted between the anode side of MEA and the current collector in place of the carbon felt.

For the evaluation of newly prepared anodes (Section 3.2), carbon current collectors were used in both the anode and the cathode of the PEAECs. As an exception, a Ti anode current collector was used in the PEAEC fabricated with IrO2-nano/Ti to unify electrode materials of the anode. For the optimization of the cathode structure (Section 3.3) and reaction conditions (Section 3.4), Ti current collectors were used to produce both the anode and the cathode to obtain larger current...
We fabricated the PEAEC having a reference electrode as depicted in Fig. 1b to determine the anode and cathode potential separately in the PEAEC operation. Ti plate having a grid (2 cm × 2 cm) with rectangular holes was used as current collector, and OX solution was flowed in the placed behind the current collector. An Ag/AgCl reference electrode was placed in the OX solution reservoir and used to estimate electrode potential. The anode potential can be calculated using the following equation [26],

\[(\text{anode potential}) = (\text{cathode potential}) + (\text{cell potential}) + IR\]  

where \(I\) equals the current density in A cm\(^{-2}\) and \(R\) is the ohmic resistance of the cell estimated using electrochemical impedance spectroscopy measurements. The anode and cathode overpotentials were calculated using the standard electrode potentials for water oxidation (1.23 V vs SHE) and for OX reduction to form GC (0.13 V vs SHE), respectively.

### 2.7. Electrochemical reduction of OX using PEAEC

OX aqueous solution (0.03–3 M, pH = 1.6–0.5) and deionized water were used as a reaction solution for cathode and anode, respectively. To avoid the influence of the O\(_2\) reduction reaction during the electrolysis, the solution was bubbled once with Argon and degassed using a degasser (Gastorr BG-34, FLM Co.) before flowing into the PEAEC. The reaction solution was introduced using a flow controller (PCS Pump SP-21, FLM Co.) on each side at a flow rate of 0.5 mL min\(^{-1}\). We performed OX reduction at 60 °C, which was the temperature optimized in the previous study.

The reduction current was monitored under application of a constant voltage in the range from 1.8 to 3.0 V between the electrodes using a potentiogalvanostat (1280 C, Solartron). Products generated during the electrolysis were analyzed using a high performance liquid chromatographic apparatus equipped with refractive index detector (Prominence, Shimadzu Co.) and a separating column for organic acids (KC-811, Shodex Co.). The Faradaic efficiency (FE) for each product was determined as follows,

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

where \(n\) represents the number of electrons required for the formation of products in OX reduction (\(n = 2\) and \(4\) for formation of GO and GC, respectively); \(m_{\text{products}}\) is the moles of products; \(F\) is Faraday constant \((96,485 \text{ C mol}^{-1})\); and \(Q\) is the total charge in Coulombs passed across the electrode during the electrolysis.

### 3. Results and discussion

#### 3.1. Preparation of IrO\(_2\)-nano

Fig. 2 compares transmission electron microscopy (TEM) images of IrO\(_2\)-micro and IrO\(_2\)-nano. We found that agglomerates larger than 1 μm in diameter are included in IrO\(_2\)-micro (Fig. 2a). Although IrO\(_2\)-nano contains agglomerates, the sizes of the agglomerates (< 200 nm, Fig. 2b) were much smaller than those of IrO\(_2\)-micro. More interestingly, large numbers of IrO\(_2\) nanoparticles with diameter of 3.7 ± 1.8 nm, which had not been reported in the Baglio’ s paper [22], were observed in the TEM images for IrO\(_2\)-nano (Fig. 2b). The specific surface area estimated for IrO\(_2\)-nano (13.2 m\(^2\) g\(^{-1}\)) was an order of magnitude smaller than that reported by Baglio et al (ca. 100 m\(^2\) g\(^{-1}\)) [22]. The origin of such a difference between our observation and reported results might be slight differences in the experimental conditions, e.g., reaction and calcination temperature. In any case, the specific surface area for IrO\(_2\)-nano (13.2 m\(^2\) g\(^{-1}\)) was significantly larger than that for IrO\(_2\)-micro (0.6 m\(^2\) g\(^{-1}\)).

Ir-L\(_{III}\) XANES spectra for Ir foil, IrO\(_2\)-micro and IrO\(_2\)-nano are shown in Fig. 3. Absorption peaks in the spectra for IrO\(_2\)-micro and IrO\(_2\)-nano were located at similar energies which were different from that
observed for Ir foil, implying that valence states of Ir species in IrO$_2$-nano are identical to that in IrO$_2$-micro, i.e., Ir$^{4+}$.

Fig. 4 provides LSV curves measured on IrO$_2$-micro/C, IrO$_2$-nano/C and IrO$_2$-nano/Ti. The overpotential required to deliver a current of 10 mA cm$^{-1}$ by IrO$_2$-nano/C was 559 mV. This value is smaller than 755 mV observed for IrO$_2$-micro/C. The drastic enhancement of catalytic activity for water oxidation may be attributed to higher specific surface area of IrO$_2$-nano although Ir-nano includes large agglomerates. Considering IrO$_2$ is an electronic conductor, agglomerates not only work as an water-oxidation catalyst but also enhance electron transfer on the anode. Furthermore, we found that 502 mV at 10 mA cm$^{-1}$ of the overpotential on IrO$_2$-nano/Ti was lower than that on IrO$_2$-nano/C. The electrical resistance of bulk Ti ($4.2 \times 10^{-5} \Omega$ cm at 20 °C) is much lower than that of bulk graphite ($2.5-5.0 \times 10^{-4} \Omega$ cm (//basal plane), $3.0 \times 10^{-1} \Omega$ cm (\basal plane) at 20 °C). Thus, catalytic enhancement on IrO$_2$-nano/Ti is possibly assigned to favorable conductivity of the Ti electrode to accelerate the charge transfer to the catalyst. Indeed, the ohmic resistance of the electrochemical cell with IrO$_2$-nano/Ti working electrode (1.67 Ω) is clearly smaller than that with IrO$_2$-nano/C (2.91 Ω).

3.2. Performance of the PEAECs employing IrO$_2$-nano applied anodes

Fig. 5 represents $I$-$V$ curves on the anode and cathode of PEAECs with IrO$_2$-micro/C or IrO$_2$-nano/Ti (OX conc.: 30 mM, cathode: TiO$_2$/Ti-M, reaction area: 4 cm$^2$, flow rate: 0.5 mL min$^{-1}$, temp.: 60 °C). When IrO$_2$-micro/C was utilized, the overpotential for the anode reaction was 750 mV (at 60 mA), which were larger than that for the cathode reaction (630 mV at 60 mA). The employment of IrO$_2$-nano/Ti anode efficiently reduced overpotential at the anode into 490 mV (at 58 mA), and
this value is clearly smaller than the cathode overpotential (600 mV at 58 mA).

Fig. 6a–c show current densities and FEs for products on the PEAEC (OX conc.: 30 mM, cathode: TiO2/Ti-M, reaction area: 4 cm2, flow rate: 0.5 mL min−1, temp.: 60 °C). The PEAEC employing IrO2-micro/C exhibited drastic degradation of the current density during the operation at 2.6 V, and did not show a linear dependence between the current density and the applied potential at the applied potential range of 2.6–3.0 V (Fig. 6a). These behaviors probably reflect the corrosive nature of the carbon paper. Indeed, we observed black precipitates, which might be decomposition products of IrO2-micro/C, in the solution collected from the anode outlet of the PEAEC during operation at 2.6–3.0 V. Obviously, the employment of the IrO2-nano greatly enhanced current density, e.g., the current density obtained in the PEAEC operations with IrO2-micro/C and IrO2-nano/C were 0.475–21.7 mA cm−2 and 4.74–237 mA cm−2, respectively (Fig. 6a,b). However, IrO2-nano/C exhibited significantly lower FE values for GC production (4.29–11.3%) compared to those on IrO2-micro/C (21.2–69.3%), suggesting that the increase in reaction rate for water oxidation at the anode could supply excess amount of proton to the cathode, which accelerates hydrogen evolution not OX reduction.

Contrary to the LSV results concerning water oxidation, 4.74–237 mA cm−2 of current density on PEAEC employing IrO2-nano/
Ti anode, was slightly increased than 3.13–266 mA cm$^{-2}$ on IrO$_2$-nano/C (Fig. 6b,c). Based on these results, the performance of the anode employing IrO$_2$-nano seems much higher than that of the cathode under the present conditions e.g., low concentration of OX (30 mM) and insufficient catalytic performance of TiO$_2$/Ti-M. Optimization of the cathode structure is, hence, required for selective production of GC.

3.3. Optimization of the cathode structure

We firstly optimized OX concentration in the cathode reaction. The PEAEC operation with 1 M OX (cathode: TiO$_2$/Ti-M, reaction area: 4 cm$^2$, flow rate: 0.5 mL min$^{-1}$, temp.: 60 °C, Fig. 7a) afforded higher FEs for GC production (29.8–98.0%) and higher current densities (26.2–493 mA cm$^{-2}$) than those with 30 mM OX (5.90–30.3%, 3.20–249 mA cm$^{-2}$, Fig. 6c). This result suggests that FE for GC production increases with increasing OX concentration of the reaction solution [21]. Surprisingly, 98.0% of FE for GC production was achieved at 1.8 V although FE values were significantly reduced to 29.8–42.6% at applied potentials higher than 2.0–3.0 V, resulting probably from the competition with the hydrogen evolution reaction. We can recognize that suppression of the hydrogen evolution is indispensable to improve the FEs for GC production at the higher applied potentials. Considering that anatase TiO$_2$ exhibits higher FE for OX reduction than metallic Ti and carbon, avoiding the contact of OX solution with metallic part of Ti electrodes seems crucial to achieve higher FE values. Then, we designed 4-type PEAEC structure by placing thinner Ti mesh or thicker Ti felt between the MEA and the current collector as shown in Fig. 8.

To make a better electrical contact between the MEA and the current collector, we inserted 4 pieces of calcined Ti mesh between the MEA and the current collector in the original cathode structure (Fig. 8a). Furthermore, we thought that TiO$_2$ layer of the calcined Ti mesh might be not thick enough to prevent contact of the solution to the electrode. Thus, we replaced 4 pieces of calcined Ti mesh with a piece of hydrothermally treated Ti felt (TiO$_2$/Ti-F), because TiO$_2$/Ti-F has a sufficient thickness to fill up the space between the MEA and the current collector, and includes large amount of TiO$_2$ on its surface than calcined Ti mesh (Fig. 8b), then the performance of the PEAEC was tested (OX conc.: 1 M, reaction area: 4 cm$^2$, flow rate: 0.5 mL min$^{-1}$, temp.: 60 °C, Fig. 7b). It is worth noting that FE values for GC

![Fig. 7. Current densities and FEs for GC and GO production during the operations of the PEAECs having four different cathode structures depicted in Fig. 8(a–d) (anode: IrO$_2$-nano/Ti, OX conc.: 30 mM, reaction area: 4 cm$^2$, flow rate: 0.5 mL min$^{-1}$, temp.: 60 °C).](image-url)

![Fig. 8. Schematic views of the PEAECs with four different cathode structures (a–d). The current collectors and the silicon gaskets are omitted for simplicity.](image-url)
production was clearly increased (46.9–55.8% at 2.0–3.0 V), indicating that the hydrogen evolution was efficiently suppressed due to thicker TiO₂ layer of TiO₂/Ti-F than that of calcined Ti mesh. On the other hand, current densities (2.47–268 mA cm⁻¹) was decreased from the values before the cathode structure alternation (2.13–367 mA cm⁻¹). The thicker TiO₂ layer might also cause a decrease in electron transfer between the current collector and the catalyst.

In our recent work, we demonstrated that the MEA prepared with TiO₂/Ti-F shows faster reaction rate as well as higher FE for GC production than that with TiO₂/Ti-M [21]. Thus, we prepared a MEA with TiO₂/Ti-F and installed it to the PEAEC having the cathode structure used in preceding examination (Fig. 8c). The performance of the PEAEC including FE for GC production (46.5–63.6 at 2.0–3.0 V) and current density (3.28–385 mA cm⁻¹) was enhanced by employment of the MEA with TiO₂/Ti-F (Fig. 7c), and this result agree with reported data [21].

When we prepared the MEA with TiO₂/Ti-F, non-negligible amount of TiO₂ peeled off from TiO₂/Ti-F during the hot press processing. The metallic Ti surface uncovered by TiO₂ probably induces hydrogen production during the PEAEC operation. Therefore, we prepared a MEA without TiO₂/Ti-F, namely, with only IrO₂-nano-loaded Naftion mem- brane and Ti paper and fabricated a PEAEC in which two pieces of TiO₂/Ti-F and the MEA were placed between two current collectors (Fig. 8d). The performance of the PEAEC is displayed in Fig. 7d. TiO₂/Ti-F without hot press processing showed improved FE for GC production (58.2–73.9% at 2.0–3.0 V) compared with hot pressed one, suggesting the suppression of hydrogen evolution.

The optimization of the cathode structure efficiently enhanced performance of the PEAEC. In particular, FE values for GC production at 2.0–3.0 V reached 58.2–73.9% by employing the cathode structure composed with 2 pieces of non-hot pressed TiO₂/Ti-F (Fig. 8d), and these values are 1.7–2 times as large as those obtained with original cathode structure (29.8–42.6%, Fig. 8a). The efficiency of energy storage in GC (ηGC) can be calculated using following equation

$$\eta_{GC} = \frac{E_{\text{GC}} \times F_{\text{GC}}}{E_{\text{appl}}}$$

(4)

where $E_{\text{appl}}$ is the applied voltage, $F_{\text{GC}}$ is the FE for GC production and $E_{\text{GC}}$ is the theoretical electrolysis voltage for the PEAEC operation (1.1 V) calculated from the standard redox potentials of GC production from OX (0.13 V) and water oxidation (1.23 V) [21]. According to this equation, $\eta_{GC}$ for the PEAEC with the most optimized cathode structure (Fig. 8d) was calculated to be 59.4% ($E_{\text{appl}} = 1.8$ V, $F_{\text{GC}} = 97.1$%) at

![Fig. 9. Conversions of OX and FEs for GC and GO production during the operations of the PEAEC with 1 M (a) or 3 M (b) OX solution (anode: IrO₂-nano/Ti, cathode: TiO₂/Ti-F without hot press x 2, reaction area: 25 cm², flow rate: 0.5 mL min⁻¹, temp.: 60 °C).]
maximum. This value is significantly higher than $\eta_{GC} = 49.6\%$ achieved in previous work [21]. In addition, although the reduction of OX in the PEAEC also afforded GO as the intermediate product, the produced amount of GO was vanishingly small. Furthermore, maximum current density of 407 mA cm$^{-2}$ (at 3.0 V) offered by the most optimized PEAEC is 7.5 times as high as that in previous work (538.3 mA cm$^{-2}$ at 3.0 V) [21] and comparable to that of commercial water electrolyzers (250–1000 mA cm$^{-2}$) [7,12].

3.4. Maximization of conversion for high-concentration OX

To increase conversion of OX, the size of cathodes was expanded from 4 cm$^2$ to 25 cm$^2$. We fabricated a PEAEC with enlarged TiO$_2$-nano/Ti or IrO$_2$-nano/Ti (5 × 5 cm$^2$) and Ti current collectors having enlarged active area from 4 cm$^2$ to 25 cm$^2$. We fabricated a PEAEC with 1 M or 3 M OX by employing the following conditions: anode: IrO$_2$-nano/Ti, cathode: non-hot pressed TiO$_2$-TiFx 2, reaction area: 25 cm$^2$, flow rate: 0.5 mL min$^{-1}$, temp: 60 °C (Fig. 9a, b). It is noteworthy that 97.9% of conversion for 1 M OX was achieved at an applied voltage of 2.6 V with moderate FE (63.0%) for GC production (Fig. 9a).

In the previous work, we had already achieved almost complete conversion of 1 M OX with 0.1 mL min$^{-1}$ of flow rate at 3.0 V using the electrodes having reaction area of 25 cm$^2$ [21]. In this work, the applied voltage required for almost complete OX conversion was reduced to 2.6 V at higher flow rate of OX solution, i.e., 0.5 mL min$^{-1}$. Furthermore, the FE for GC production was drastically improved from 31.9%–63.0%. These results demonstrate that the performance of the PEAEC, including not only reaction rate but also product selectivity, was excellently enhanced in this study. Even more surprisingly, the PEAEC almost completely converted 3 M OX (98.9% conversion) at an applied voltage of 2.8 V with reasonable FE (66.6%) for GC production. In this condition, the maximum $\eta_{GC}$ value is estimated to be 53.6% ($E_{app} = 1.8\text{ V}, F_{GC} = 87.9\%$). Among the typical electrical energy storage devices [27], water electrolyzers [7,12], and redox flow batteries [28–31] are the more advanced devices than PEAEC. We estimated the volumetric energy storage capacity of 3 M OX solution to be 321 Ah L$^{-1}$. This value is almost 150 times higher than that of gaseous hydrogen (2.2 Ah L$^{-1}$ (SATP)) and approximately 5 times higher than that of vanadium-based electrolyte used in the redox flow batteries (60 Ah L$^{-1}$) [31]. We believe further improvement of PEAEC promotes its potential as an efficient energy storage device.

4. Conclusion

The performance of the flow-type PEAEC continuously converting OX into GC was drastically improved through two different approaches involving development of an active and durable titanium anode employing nanoscale TiO$_2$ and optimization of PEAEC structures. Fully reconstructed PEAEC achieved continuous conversion of 3 M OX, which is an almost saturated aqueous solution at 60 °C, into GC with almost 100% of OX conversion (98.9%) at an applied potential of 2.8 V. The energy conversion efficiency using the PEAEC was significantly increased in this study ($\eta_{GC} = 59.4\%$, $E_{app} = 1.8\text{ V}, F_{GC} = 97.1\%$). These efforts will contribute to the earliest realization of practical utilization of renewable electricity for the sustainable energy circulation.

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