


 Cite this: *RSC Adv.*, 2021, 11, 11224

H₂O₂ production on a carbon cathode loaded with a nickel carbonate catalyst and on an oxide photoanode without an external bias†

 Soichi Takasugi,^a Yugo Miseki,^a Yoshinari Konishi,^a Kotaro Sasaki,^b Etsuko Fujita^b and Kazuhiro Sayama^{*a}

Efficient H₂O₂ production both on a carbon cathode modified with various metal salts and on an oxide photoanode was investigated. The cathodic current density and faradaic efficiency for H₂O₂ production (FE(H₂O₂)) on a carbon cathode in KHCO₃ aqueous solution were significantly improved by the loading of an insoluble nickel carbonate basic hydrate catalyst. This electrode was prepared by a precipitation method of nickel nitrate and KHCO₃ aqueous solution at ambient temperature. The nickel carbonate basic hydrate electrode was very stable, and the accumulated concentration of H₂O₂ was reached at 1.0 wt% at a passed charge of 2500C (the average FE(H₂O₂) was 80%). A simple photoelectrochemical system for H₂O₂ production from both the cathode and a BiVO₄/WO₃ photoanode was demonstrated without an external bias or an ion-exchange membrane in a one-compartment reactor under simulated solar light. The apparent FE(H₂O₂) from both electrodes was calculated to be 168% in total, and the production rate of H₂O₂ was approximately 0.92 μmol min⁻¹ cm⁻². The solar-to-chemical energy conversion efficiency for H₂O₂ production (STC_{H₂O₂}) without an external bias was approximately 1.75%.

 Received 8th February 2021
 Accepted 27th February 2021

DOI: 10.1039/d1ra01045j

rsc.li/rsc-advances

Introduction

Hydrogen peroxide (H₂O₂) is an environmentally friendly and important chemical oxidant that has been widely applied to pulp bleaching, waste treatment, chemical synthesis of peroxides, and food sterilization.^{1–8} The anthraquinone redox process using H₂ and O₂ gases has been used for the industrial large-scale production of H₂O₂.^{2,9} However, there are many problems in this process: a large amount of energy requirement and H₂ consumption in the complicated system producing a huge amount of CO₂ emission, the usage of harmful organic solvents, the requirement of concentration, and transformation from the central process to consumption area. Therefore, some distributed and small-scale electrochemical H₂O₂ production processes in aqueous solution have been widely investigated.^{5,10–22} The on-site electrochemical process has many advantages, such as safety without H₂ usage, no organic solvent separation, and controllability on the production amount and concentration for demand. Two kinds of reactions for H₂O₂ production are present in the

electrochemical process: reductive H₂O₂ production from O₂ on a cathode (eqn (1)), and oxidative H₂O₂ production from H₂O on an anode (eqn (2)).

There are many reports on the reductive H₂O₂ production from O₂.^{23–30} In contrast, the oxidative H₂O₂ production and accumulation from H₂O are very difficult. However, we and others have reported that H₂O₂ can be accumulated when KHCO₃ aqueous solution is used in electrochemical and photoelectrochemical processes.^{19–22,31–35} It is advantageous and highly efficient to produce H₂O₂ on both electrode sides by combining the cathodic and anodic reactions, as shown in eqn (3), compared to the production on each electrode side under the same electric charge. The apparent faradaic efficiency for the H₂O₂ production (FE(H₂O₂)) could reach 200% in total (100% + 100%) if the production occurred on both sides of the electrode.³⁶ We have previously demonstrated that the H₂O₂ production can take place on a BiVO₄/WO₃ photoanode and an Au cathode at near-neutral pH in KHCO₃ aqueous solution using a simple one-compartment cell without an external bias, as shown in Fig. 1.¹⁹ The apparent faradaic efficiency was 140% in total (FE(H₂O₂) = 90% and 50% on the Au cathode and the BiVO₄/WO₃ photoanode, respectively). The band gap of BiVO₄ is 2.4 eV, and the theoretical maximum photocurrent is reported to be 7.5 mA cm⁻².³⁷ Unfortunately, the current density of the Au cathode, a novel metal electrode, was low (−0.18 mA cm⁻² at +0.5 V (vs. RHE)). Therefore, improved systems are needed for practical applications.

^aGlobal Zero Emission Research Center (GZR), National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan. E-mail: k.sayama@aist.go.jp

^bChemistry Division, Brookhaven National Laboratory, Upton, New York, 11973-5000, USA

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1ra01045j



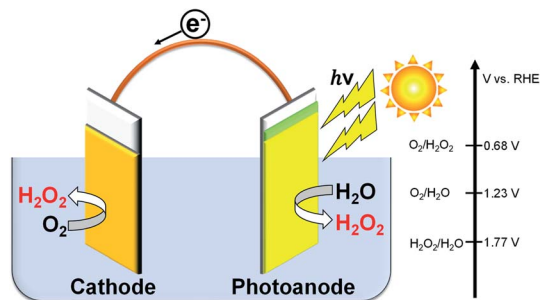
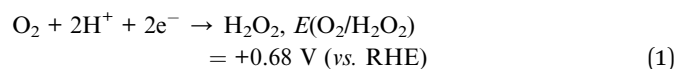
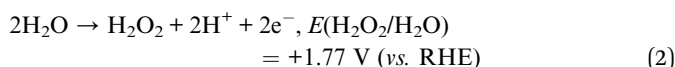


Fig. 1 H_2O_2 production on both electrode sides in a one-compartment cell under illumination without an external bias or an ion-exchange membrane.

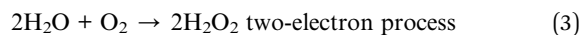
Cathode reaction:



Anode reaction:



Eqn (1) + (2)



As for noble-metal-free cathodes, there are several reports on the use of carbon-based materials modified with inexpensive metal compounds mainly at basic pH.^{38–41} However, efficiencies for the H_2O_2 production with these cathodes were low at near-neutral pH, and an ion-exchange membrane was essential when the pH values of the anodic and cathodic electrolyte solutions were different.^{21,22} Recently, we reported that a carbon cathode modified with a biomass-derived W-based electrocatalyst exhibited a relatively high cathodic current for the reductive H_2O_2 production in a near-neutral KHCO_3 aqueous solution in a two-compartment cell, but the $\text{FE}(\text{H}_2\text{O}_2)$ and the partial current density for H_2O_2 production were not enough.²⁰

In this paper, we pursued developing more efficient H_2O_2 production systems on a photoanode and a noble-metal-free cathode in a KHCO_3 aqueous solution without an ion-exchange membrane or an external bias in a one-compartment cell. The system using a single electrolyte in a one-compartment cell without any membrane is very simple. It was found that nickel carbonate on a carbon-based cathode showed excellent electrocatalytic activity on both $\text{FE}(\text{H}_2\text{O}_2)$ and the partial current density for H_2O_2 production in a KHCO_3 solution. A water-insoluble nickel carbonate electrocatalyst was easily prepared *in situ* from a nickel salt and KHCO_3 aqueous solution at ambient and mild conditions. The apparent solar-to-chemical energy conversion efficiency for H_2O_2 production ($\text{STC}_{\text{H}_2\text{O}_2}$) on a combination system of the $\text{BiVO}_4/\text{WO}_3$ photoanode and the cathode loaded with nickel carbonate electrocatalyst without external bias reached 1.75%, which is the highest among all reported values so far.

Experimental section

Fabrication of the carbon cathode loaded with various metals

A water-repellent-treated carbon paper (abbreviated as CP; 1.0 cm^2 , TORAY, TGP-H-090) was used as the substrate plate of the cathode. A conductive carbon powder of Ketjenblack EC600JD (abbreviated as KB; Lion Specialty Chemicals Co., Ltd.)^{42–44} was used with various electrocatalysts on CP. KB powder loaded with various metal salts as an electrocatalyst (abbreviated as Met/KB) was prepared by an impregnation method. The metal salts used were Cr(II) nitrate nonahydrate, Mn(II) nitrate tetrahydrate, Fe(III) nitrate nonahydrate, Co(II) nitrate hexahydrate, Ni(II) nitrate hexahydrate, Cu(II) nitrate trihydrate, Zn(II) nitrate hexahydrate, Ga(III) nitrate *n*-hydrate, hexaammonium heptamolybdate tetrahydrate, and ammonium tungstate *para*-penta-hydrate (purchased from Fujifilm Wako Pure Chemicals Corporation).

A mixture of 100 mg of KB powder and 0–1000 mg of various metal salts was added to 20 mL of H_2O . The suspension was thoroughly dispersed by ultrasonication for 30 min and dried overnight in a heating oven at 353 K under an ambient pressure. The ratio of a loaded metal salt of *x* wt% to the weight of the KB powder was abbreviated as Met_x/KB . For example, a loaded metal salt of 10 and 100 wt% vs. the weight of the KB powder were abbreviated as $\text{Met}_{10}/\text{KB}$ and $\text{Met}_{100}/\text{KB}$, respectively. A mixture of 1.5 mg (standard amount) of the electrocatalyst (KB, Met/KB) and 0.75 mg of 20 wt% Nafion solution (Sigma-Aldrich Co., USA) was dispersed in 0.5 mL of ethanol, and loaded on one side of the CP substrate (area 1.0 cm^2) at room temperature. This cathode loaded with an electrocatalyst and KB powder on CP was dried at 333 K for 30 min in a heating oven.

HNO_3 treatment for KB powder

HNO_3 -treated KB powder (abbreviated as KB_{HNO_3}) was prepared by an immersion process. To 38.3 g of concentrated HNO_3 aqueous solution (60%, Fujifilm Wako Pure Chemical Corporation), 1000 mg of KB powder was added. The suspension was thoroughly heated at 353 K for 24 h with a string at 300 rpm in a heating oven. They were collected by suction filtration and thoroughly washed with distilled water. Metal-salt loading on KB_{HNO_3} (abbreviated as $\text{Met}/\text{KB}_{\text{HNO}_3}$) was prepared and coated on CP as the cathode by the same process.

Fabrication of the $\text{BiVO}_4/\text{WO}_3$ photoelectrode

The $\text{BiVO}_4/\text{WO}_3$ photoelectrode used in this study was synthesized using the method previously reported by Fuku,⁴⁵ and was prepared on a F-doped SnO_2 (FTO) glass substrate by spin-coating method. The precursor of the WO_3 layer was loaded by spin coating (1000 rpm, 15 s, 200 μL per 12 cm^2) on FTO, and then calcined at 773 K for 30 min. Spin coating of the WO_3 layer was repeated twice using *N,N*-dimethylformamide (DMF) solutions of tungsten hexachloride (WCl_6 , 4 N; Kojundo Chemical Laboratory, Co., Ltd.) adjusted to 504 and 252 mM for the first and second coat, respectively. The BiVO_4 layer was also fabricated by spin coating (500 rpm, 15 s, 400 μL per 12 cm^2) on the WO_3 layer, and calcined at 773 K for 30 min. The spin coating of



the BiVO₄ layer was repeated three times using 0.4 or 0.6 M BiVO₄ precursor solution. The first layer of BiVO₄ used 0.4 M BiVO₄ precursor solution, and the rest of the layer used 0.6 M solution. The BiVO₄ precursor solution, adjusted to 100 mM, was prepared by dissolving bismuth oxide (BiO_{1.5}) solution (Symmetrix Co., USA) and a vanadium oxide (VO_{2.5}) solution (Symmetrix Co., USA) in butyl acetate with a Bi/V molar ratio of 1.0. To the BiVO₄ solution, 10 wt% butyl acetate solution of ethyl cellulose was added as a thickening agent with a (BiVO₄ solution)/(ethyl cellulose solution) volume ratio of 1.5.

Electrochemical measurements and quantification method

Electrochemical measurement on the cathode

The electrochemical properties of the electrocatalyst cathode were evaluated in a 2.0 M KHCO₃ aqueous solution (pH 8.8) with O₂ bubbling (50 mL min⁻¹) with an ice bath (273–278 K) by using an electrochemical analyzer (Hokuto Denko, HZ-7000). The current–potential (*I*–*E*) characteristics were measured *via* a three-electrode method using a two-compartment cell. The scan rate was set at 2 mV s⁻¹. The volume of the electrolyte solutions of the anode and cathode chambers was 35 mL with stirring. The reference electrode used was 3 M Ag/AgCl, and the counter electrode was a Pt wire. Between the anode and cathode chambers, Aciplex (Asahi KASEI) was used as an ion-exchange resin. After the reaction was completed, 1.1 mL of the reaction solution was taken out using a syringe. The schematic illustration of a two-compartment cell is shown in Fig. S1(a).† All potentials in this paper were quoted with respect to the reversible hydrogen electrode (RHE), according to the Nernst equation (eqn (4)).

$$E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.0591 \times \text{pH} + 0.197 \quad (4)$$

An accumulation experiment for H₂O₂ was conducted at a constant applied bias of +0.5 V vs. RHE.

Simultaneous H₂O₂ production on both the photoanode and cathode without an external bias or membrane

The simultaneous production of H₂O₂ from H₂O oxidation at the photoanode and O₂ reduction at the cathode was performed without applying any external bias using a two-electrode system composed of a BiVO₄/WO₃ photoanode (irradiation area of 0.2 cm² with a white board behind the photoanode) and a Ni₁₀/KB_{HNO₃} cathode (catalyst loading 1.5 mg cm⁻², area 0.2 cm²). An aqueous solution of KHCO₃ (2.0 M) was used as an electrolyte (200 mL), and CO₂ and O₂ gases were each bubbled for 50 mL min⁻¹ into the one-component cell with a pH value of 8.0 in an ice bath (273–278 K). An ice bath was used under CO₂ bubbling to obtain the optimum reaction conditions for the stability of the photoanode. It was confirmed that O₂ gas diffusion is not the rate-limiting factor under our conditions of <10 mA cm⁻². A solar simulator calibrated to AM 1.5G (1 SUN, 0.1 W cm⁻²) was used as the light source. The schematic

illustration of our reaction system in a one-compartment cell without membrane is shown in Fig. S1(b).†

Characterization and quantification method

The prepared electrodes were characterized by X-ray fluorescence (XRF, Rigaku, Super mini200) measured in a vacuum with a wavelength dispersive spectrometer with Pd–K radiation. The crystal structures of the samples were investigated by X-ray diffraction (XRD, Malvern Panalytical, Empyrean) using Cu K α radiation at 40 kV and 40 mA. Transmission electron microscopy and energy dispersive X-ray spectroscopy (TEM and EDS, Philips, Tecnai Osiris) measurements were carried out with a field emission gun operating at 200 kV.

The amount of produced H₂O₂ was quantified *via* UV-visible spectroscopy (TECAN, Infinite 200 PRO). Then, 1.0 mL of sample was added to 0.9 mL of 3.0 M HCl aqueous solution and 0.1 mL of FeCl₂ in 1.0 M HCl aqueous solution and quantified from Fe³⁺ colorimetry ($\lambda = 330$ nm), as we reported previously.^{19,20,32,44} The faradaic efficiency for H₂O₂ production (FE(H₂O₂)) was calculated using eqn (5):

$$\text{FE}(\text{H}_2\text{O}_2)\% = [\text{amount of produced H}_2\text{O}_2] \times 100 \times 2 / [\text{amount of passed electrons}] \quad (5)$$

We confirmed that the error range of the FE(H₂O₂) value was around $\pm 2\%$.

The apparent partial current density for H₂O₂ production at a constant potential ($J_{\text{ap}}(\text{H}_2\text{O}_2)$) was calculated using eqn (6):

$$J_{\text{ap}}(\text{H}_2\text{O}_2) = J(\text{Total}) \times \text{FE}(\text{H}_2\text{O}_2) \quad (6)$$

Here, $J(\text{Total})$ is the total current density at a constant potential and FE(H₂O₂) is the average faradaic efficiency at the passed charge of a constant potential. $J_{\text{ap}}(\text{H}_2\text{O}_2)$ represented the actual H₂O₂ production rate.

The turnover number was calculated using eqn (7). The amount of nickel was measured by XRF.

$$\text{Turnover number} = [\text{amount of produced H}_2\text{O}_2 \text{ (in moles)}] / [\text{amount of nickel (in moles)}] \quad (7)$$

The apparent solar-to-chemical energy conversion efficiency (STC) for the H₂O₂ and O₂ production on the BiVO₄/WO₃ photoanode (irradiation area of 0.2 cm² with a white board behind the photoanode) and on the Ni₁₀/KB_{HNO₃} cathode (catalyst loading 1.5 mg cm⁻², area 0.2 cm²) was calculated using eqn (8):³⁵

$$\text{STC}_{\text{H}_2\text{O}_2}(\%) = [(V_{\text{H}_2\text{O}_2} \times \Delta G) \times 100] / \text{Int} \quad (8)$$

$V_{\text{H}_2\text{O}_2}$ is the H₂O₂ production rate (in moles per second per square centimeter), ΔG is the Gibbs free energy from eqn (3) ($\Delta G = +116.8$ kJ mol⁻¹),⁴⁶ and Int is the intensity of the incident simulated solar light (0.1 W s⁻¹ cm⁻²).

Results and discussion

Table 1 shows the $J(\text{Total})$ and the FE(H₂O₂) through a O₂ reduction reaction on the KB/CP substrate cathodes modified



Table 1 FE(H₂O₂), J(Total), and J_{ap}(H₂O₂) of Met₁₀₀/KB and Met₁₀/KB cathodes

Met/KB ^a	FE(H ₂ O ₂) ^b /%	J(Total) ^c /mA cm ⁻²	J _{ap} (H ₂ O ₂)/mA cm ⁻²
CP substrate only	—	5.4 × 10 ⁻⁴	—
KB	59	-4.0	-2.4
Fe ₁₀₀ /KB	4	-11.5	-0.4
Fe ₁₀ /KB	13	-10.5	-1.4
Cu ₁₀₀ /KB	9	-8.5	-0.8
Cu ₁₀ /KB	42	-8.5	-3.6
Cr ₁₀₀ /KB	32	-5.1	-1.6
Cr ₁₀ /KB	43	-6.2	-2.9
Mn ₁₀₀ /KB	1	-4.2	-0.04
Mn ₁₀ /KB	3	-5.2	-0.2
Co ₁₀₀ /KB	20	-3.3	-0.7
Co ₁₀ /KB	15	-8.9	-1.3
Ga ₁₀₀ /KB	54	-3.5	-1.9
Ga ₁₀ /KB	56	-5.4	-3.0
W ₁₀₀ /KB	33	-4.6	-1.5
W ₁₀ /KB	44	-6.9	-3.0
Mo ₁₀₀ /KB	36	-3.7	-1.3
Mo ₁₀ /KB	67	-5.0	-3.4
Ni ₁₀₀ /KB	66	-5.3	-3.5
Ni ₁₀ /KB	85	-8.1	-6.9
Zn ₁₀₀ /KB	71	-4.4	-3.1
Zn ₁₀ /KB	65	-6.9	-4.5

^a Met₁₀₀/KB or Met₁₀/KB: various metal salts loaded on KB powder (100 or 10 wt% of the loading amount of precursor metal salt (Met) vs. KB powder). ^b The FE(H₂O₂) was measured at the passed charge after 5C. ^c The J(Total) was measured at a constant potential of +0.5 V (vs. RHE).

with various metal salts (Met₁₀₀/KB and Met₁₀/KB, 100 and 10 wt% of metal salt in KB powder) in a 2.0 M KHCO₃ aqueous solution under O₂ bubbling condition. Here, FE(H₂O₂) and J_{ap}(H₂O₂) were evaluated at the passed charge after 5C at +0.5 V. The J(Total) of the CP substrate was negligibly small. On the other hand, the J(Total) largely increased when KB powder was loaded on the CP substrate. KB powder has a high surface area (1270 m² g⁻¹) and high conductivity.⁴⁷ It was surmised that the electron could be transferred through the conductive KB

powder network, and that the reduction for H₂O₂ production could take place on the KB surface. The optimum loading amount of KB powder on the CP substrate was around 1.5 mg cm⁻², and the current did not increase by further loading (Fig. S2†). The exfoliation of the powder from the CP substrate was observed by overloading (Fig. S2d†). Therefore, the loading amount of Met₁₀/KB and Met₁₀₀/KB on the CP substrate was fixed at 1.5 mg cm⁻² in all experiments. The values of J(Total), FE(H₂O₂) and J_{ap}(H₂O₂) were changed by the modification of

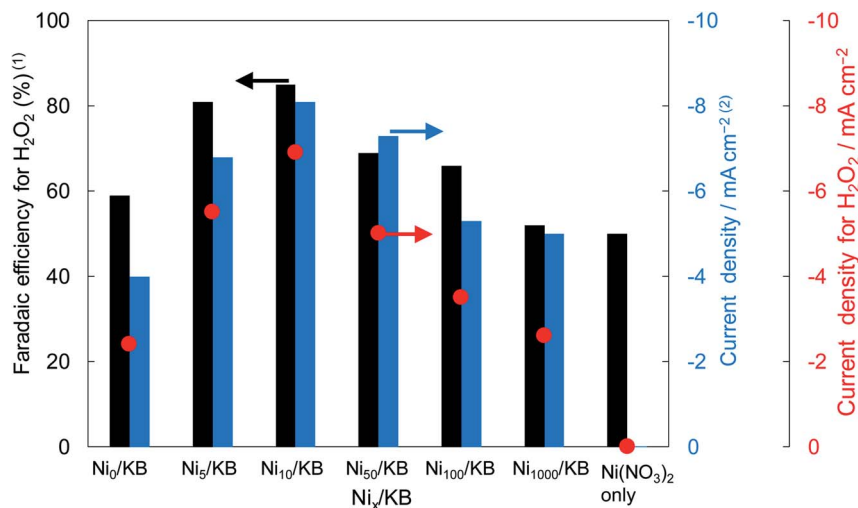


Fig. 2 The FE(H₂O₂), J(Total), and J_{ap}(H₂O₂) using various amounts of Ni nitrate on the KB cathode. The value of x (in weight percent) in Ni_x/KB was the loading amount of Ni(NO₃)₂ vs. pristine KB powder. The FE(H₂O₂) was measured at the passed charge after 5C. The J(Total) was measured at a constant potential of +0.5 V (vs. RHE).



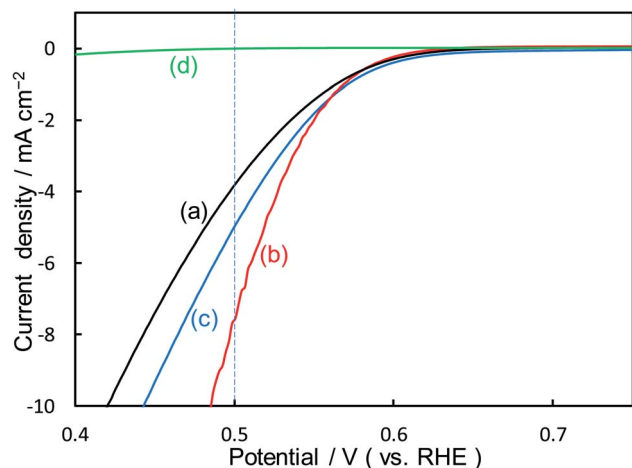
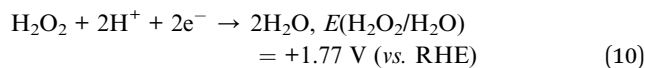
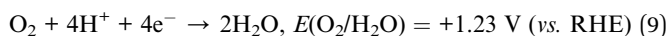


Fig. 3 *I*-*E* curves of (a) pristine KB powder, (b) Ni₁₀/KB cathode, (c) Ni₁₀₀/KB cathode, (d) Ni nitrate only without KB powder at a scan rate of 2 mV s⁻¹.

various metal salts on the KB cathode. FE(H₂O₂) decreased by modification of Fe, Cu, Cr, Mn, Co, Ga, or W, compared to pristine KB powder and increased by modification with Mo₁₀₀/KB, Ni₁₀₀/KB, Ni₁₀/KB, Zn₁₀₀/KB, and Zn₁₀/KB. As for the *J*(Total), most of the total current was improved by modification of these metal salts. The two-electron reduction for the H₂O₂ production reaction from O₂ (eqn (1)) was competitive with other undesirable reactions: four-electron reduction of O₂ to H₂O (eqn (9)) and successive reduction of H₂O₂ to H₂O (eqn (10)).



The theoretical reduction potentials of the four-electron reduction of O₂ (+1.23 V, eqn (9)) and successive reduction of H₂O₂ (+1.77 V, eqn (10)) were significantly positive compared to

that of H₂O₂ production *via* two-electron reduction of O₂ (+0.68 V, eqn (1)). In the case of the *J*(Total) improvement with decreasing FE(H₂O₂), the *J*_{ap}(H₂O₂) was not significantly improved. It was surmised that these undesirable reactions might be accelerated by the modification of these metal nitrates or ammonium salt of Cu, Cr, Mn, Co, Ga, W, and Mo. On the other hand, the *J*(Total) and FE(H₂O₂) were both increased when Ni or Zn nitrate was modified. In particular, the Ni₁₀/KB cathode showed the highest performance of *J*_{ap}(H₂O₂) on the H₂O₂ production (-6.9 mA cm⁻²) among all metal salts in Table 1. The *J*_{ap}(H₂O₂) was also improved by modification of all various Ni salts (nitrate, sulfate, acetate, chloride, Ni oxide, Ni hydroxide, and nickel carbonate (Table S1,† 10 wt% of Ni salt)), suggesting that the positive effect of the current density and the FE(H₂O₂) was caused mainly by the presence of Ni salt itself, rather than by the effect of anions. Ni nitrate showed the highest activity among them. Then, Ni nitrate was mainly used as a precursor for loading to a carbon electrode for subsequent experiments. An improved effect of the NiO-loaded KB cathode was not obvious compared to those with other nickel salts. NiO particles are hardly soluble in aqueous solution. In the case of soluble nickel-salts loaded KB cathodes, their properties were positively changed through the process of dissolution and precipitation. In the case of NiO, the bulk of NiO may be not changed in KHCO₃ solution.

Fig. 2 shows the dependence of the loading amount of Ni nitrate over the KB cathode on FE(H₂O₂), *J*(Total), and *J*_{ap}(H₂O₂). All values of the FE(H₂O₂), *J*(Total), and *J*_{ap}(H₂O₂) showed volcano shape profiles, depending on the amount of Ni nitrate modification, and had the best values at 10 wt% of Ni nitrate on the KB cathode (Ni₁₀/KB). As for the Ni-nitrate-loaded cathode without KB powder (the rightmost data in Fig. 2), the *J*(Total) and the *J*_{ap}(H₂O₂) were very small, while the FE(H₂O₂) was equivalent to pristine KB powder. The current-potential dependences of some typical cathodes with and without Ni nitrate are shown in Fig. 3. It was surmised that the loaded nickel compound itself on the CP substrate might be hardly conductive, and the excess amount of Ni compound hindered the electron transfer through the network of the conductive KB.

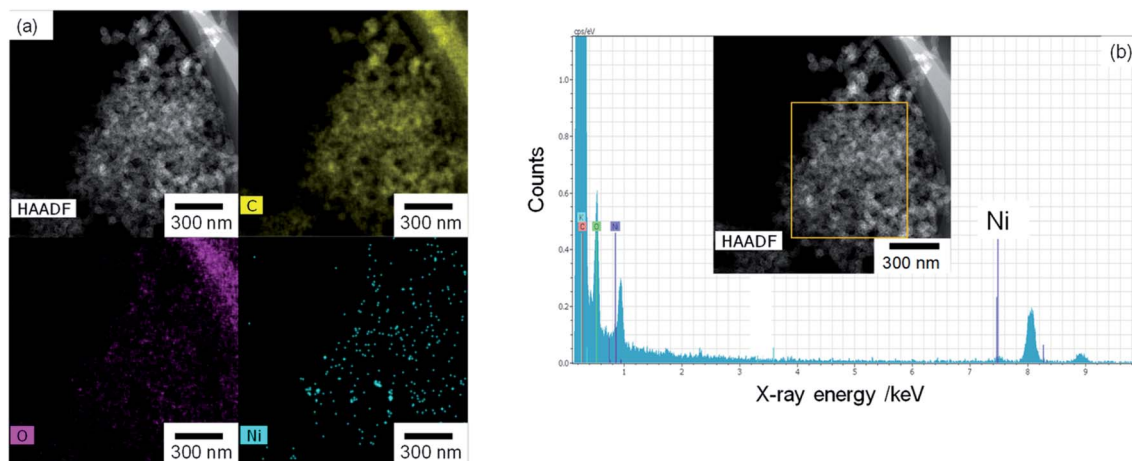


Fig. 4 Ni₁₀/KB images: (a) HAADF-TEM image and element mapping images of EDX. (b) EDX spectrum and analysis area (yellow square).



Table 2 Amount of Ni compound on the KB cathode as measured by XRF

	Pristine KB	Ni ₁₀ /KB	Ni ₁₀₀ /KB
Amount of Ni/$\mu\text{g cm}^{-2}$			
Before washing	0	2.6	24.5
Washing with distilled water	0	0	0
Washing with 2.0 M KHCO ₃	0	2.3	20.2

The TEM and EDX images of Ni₁₀/KB are shown in Fig. 4. The Ni₁₀/KB sample was prepared by immersion in KHCO₃ electrolyte. Although it was difficult to recognize the clear particle shapes of the Ni compounds based on a TEM image only, the presence of a small aggregation of Ni element was confirmed by TEM-EDX image analysis. The aggregation size of the Ni compounds was approximately 10–40 nm in the EDX mapping images. On the other hand, when a larger amount of Ni was loaded (Ni₁₀₀/KB), a large aggregation (>0.5 μm) of the Ni element was observed by SEM-EDX measurements (Fig. S3†). It was speculated that the large aggregation of the Ni compounds might decrease the current density at a higher loading amount of Ni(NO₃)₂ \cong 50 wt% in Fig. 2.

The Ni amount with KB powder (Ni₁₀/KB and Ni₁₀₀/KB) measured by XRF before and after washing with distilled water or KHCO₃ aqueous solutions is shown in Table 2. The Ni signal by XRF before the washing process completely disappeared after washing with distilled water. On the other hand, after washing with KHCO₃ aqueous solution, the Ni signal was clearly detected, and more than 80% of Ni remained on the KB cathode. Ni(NO₃)₂ is easily dissolved in water, while nickel carbonates have a very poor water solubility (solubility product ($\text{p}K_{\text{sp}}$) = 11.2).⁴⁸ Actually, the green transparent aqueous solution of Ni(NO₃)₂ changed to colorless by the addition of KHCO₃, and insoluble green powders were precipitated (Fig. S4†). The positive effect of Ni loading on the *I*-*E* curve disappeared by washing with distilled water, not by washing with a bicarbonate solution (Fig. S5†). Moreover, the presence of Ni species on the surfaces of the cathodes was also investigated by XPS (Fig. S6†). The peaks of the spectrum of Ni2p_{3/2} and Ni2p_{5/2} were observed on Ni₁₀/KB (a) before and (b) after washing with KHCO₃ aqueous solution. However, they were not observed (c) after washing with distilled water. While the apparent surface coverage of Ni compounds to carbon before washing with KHCO₃ aqueous solution as calculated by XPS intensity was not large (less than 1%), the exact Ni coverage was difficult to estimate due to the low sensitivity and presence of carbon impurities.

We compared our electrocatalyst powder sample with reference reagents of nickel(II) carbonate basic hydrate (NiCO₃·2Ni(OH)₂·4H₂O; Fujifilm Wako Pure Chemical Corporation, 44% as Ni), nickel(II) hydroxide (Ni(OH)₂; Fujifilm Wako Pure Chemical Corporation, 95%) and nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O; Fujifilm Wako Pure Chemical Corporation, 99.9%) using XRD and thermogravimetric-differential thermal analysis (TG-DTA). Our synthetic powder sample was prepared by immersing Ni(NO₃)₂ in a KHCO₃ aqueous solution. As shown in the XRD patterns (Fig. 5), the shape and the broad peak

position at around 17° and 35° of our powder sample were similar to those of the reference nickel carbonate rather than Ni(OH)₂. In the TG-DTA results (Fig. S7†), the curves of TG and DTA of our electrocatalyst sample (a) were very similar to those of the reference reagent of NiCO₃·2Ni(OH)₂·4H₂O (b), but different from those of Ni(OH)₂ (c) and Ni(NO₃)₂·6H₂O (d). Therefore, it was concluded that the loaded Ni(NO₃)₂ on the KB cathode was immediately changed to insoluble nickel(II) carbonate basic hydrate when the cathode electrode was soaked in a KHCO₃ solution, and that the small particles (10–40 nm) of Ni carbonate formed by this process can function as an excellent catalyst for H₂O₂ production on the KB cathode. This simple preparation of the insoluble electrocatalyst at ambient conditions is a significant advantage for practical applications.

We confirmed that the H₂O₂ production properties on FE(H₂O₂) and *J*_{ap}(H₂O₂) over Ni₁₀/KB were almost the same as those over pristine KB in KOH and potassium hydrogen phosphate aqueous solution, suggesting that a positive nickel salt effect was not observed in KOH and potassium hydrogen phosphate aqueous solution, in contrast with the KHCO₃ aqueous solution. The particle of nickel carbonate basic hydrate was stable and insoluble in KOH (pH > 14) and potassium hydrogen phosphate (pH > 8.5, which is the same as KHCO₃) aqueous solution. The surface condition is very important for electrocatalytic reactions. The loaded Ni(OH)₂ on KB could show a positive effect in KHCO₃ aqueous solution, as shown in Table 1. It was confirmed using XPS measurement that the surface carbonate was reduced after the immersion in KOH or potassium hydrogen phosphate aqueous solution. From all results, it is speculated that the nickel adsorbed with carbonate, rather than nickel element itself, on the outermost surface and at the interface of the loaded electrocatalyst with KB possibly being the active site for H₂O₂ production.

It has been reported that the activity of a carbon-based cathode for H₂O₂ production from O₂ could be improved by nitric acid treatment, where the carbon surface was changed in concentrated nitric acid for a long time at high temperature.^{49,50} Therefore, we tried to combine nitric acid treatment and Ni carbonate effect on the KB cathode (abbreviated as Ni/KB_{HNO₃}).

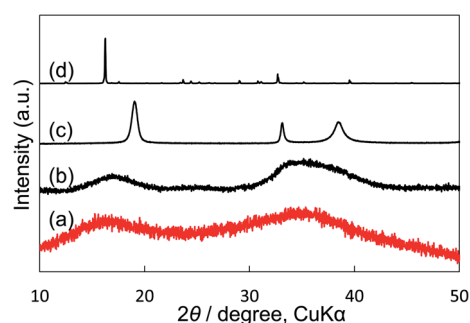


Fig. 5 XRD patterns of (a) our synthetic sample prepared by precipitation with Ni(NO₃)₂ and KHCO₃ aqueous solution. (b) Reagent powder of nickel(II) carbonate basic hydrate (NiCO₃·2Ni(OH)₂·4H₂O) as reference. (c) Reagent powder of nickel(II) hydroxide (Ni(OH)₂) as reference. (d) Reagent powder of nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) as reference. KB powder was not mixed.



Table 3 FE(H₂O₂), *J*(Total), and *J*_{ap}(H₂O₂) of nitric acid treatment and Ni loading on the KB cathodes

	FE(H ₂ O ₂) ^a /%	<i>J</i> (Total) ^b /mA cm ⁻²	<i>J</i> _{ap} (H ₂ O ₂)/mA cm ⁻²
Ni ₁₀ /KB	85	-8.1	-6.9
Ni ₁₀ /KB _{HNO₃}	82	-12.0	-9.8
KB _{HNO₃}	78	-8.9	-6.9
KB	59	-4.0	-2.4

^a The FE(H₂O₂) was measured at the passed charge after 5C. ^b The *J*(Total) was measured at a constant potential of +0.5 V (vs. RHE).

Table 3 shows the *J*(Total), FE(H₂O₂), and *J*_{ap}(H₂O₂) for the O₂ reduction reaction to H₂O₂ on KB_{HNO₃} and Ni₁₀/KB_{HNO₃}. All values of the FE(H₂O₂), *J*(Total), and *J*_{ap}(H₂O₂) of KB_{HNO₃} were improved by the nitric acid treatment compared to those when the pristine KB was used. Moreover, the *J*(Total) and *J*_{ap}(H₂O₂) of KB_{HNO₃} were improved by the loading of Ni carbonate (Ni₁₀/KB_{HNO₃}), and the *J*_{ap}(H₂O₂) reached -9.8 mA cm⁻² at +0.5 V vs. RHE. The *J*(Total) and *J*_{ap}(H₂O₂) of Ni₁₀/KB_{HNO₃} were higher compared to those of Ni₁₀/KB, suggesting the synergistic effect of nitric acid treatment and Ni carbonate catalyst.

Fig. 6 shows the dependence of the FE(H₂O₂) on the applied potentials for Ni₁₀/KB_{HNO₃}. The FE(H₂O₂) increased with the applied potential positively, and this behavior was similar to those in previous reports of carbon-based cathodes in KOH.⁵¹ The highest FE(H₂O₂) at 5C was 82–84% at around +0.5 to +0.6 V (vs. RHE). We also measured faradaic efficiency by the rotating ring disk electrode (RRDE) method (Fig. S8[†]), and found that the value of the FE(H₂O₂) by the RRDE method was 85% at +0.5 V (vs. RHE), which was almost consistent with the results of the accumulated H₂O₂ after passing 5C electrons of using a Fe³⁺ colorimetry method. The production rates of H₂O₂ on Ni₁₀/KB_{HNO₃} at +0.5 and +0.2 V (vs. RHE) were 121.9 and 330.3 mmol L⁻¹ h⁻¹ g⁻¹ cm⁻², respectively. To the best of our knowledge, these rates for reductive H₂O₂ production were the highest among all reports on noble-metal-free cathodes in aqueous solutions having near-neutral pH (Table S2[†]). Fig. 7 shows the long-term evaluation result of H₂O₂ production on the Ni₁₀/

KB_{HNO₃} cathode with large amounts of passed charge. H₂O₂ production was increased linearly at a constant applied bias at +0.5 V (vs. RHE), and the FE(H₂O₂) was around 80% passing charges up to 2500C, suggesting that the produced H₂O₂ was not further reduced to H₂O sequentially (eqn (10)) for a long term. From the linear production and the agreement of the FE(H₂O₂) by colorimetry and RRDE methods for long- and short-term quantitative measurements, respectively, we concluded that the total H₂O₂ selectivity was determined by the initial H₂O₂ selectivity on the cathode with the electrocatalyst. The amount of the produced H₂O₂ was 10.4 mmol and the amount of nickel was 0.037 μmol cm⁻² (calculated from XRF) using Ni₁₀/KB_{HNO₃}. Therefore, the turnover number was calculated as more than 14 000 from eqn (7). The H₂O₂ accumulation concentration reached 1.0 wt% in 35 mL of 2.0 M KHCO₃ aqueous solution. In addition, the *I*-*E* curves of the cathode hardly changed even after repeated 150 cycles of *I*-*E* measurements during 36 h (Fig. S9[†]), and the cathodic current remained around -11 mA cm⁻², suggesting that the modification effect of the Ni₁₀/KB_{HNO₃} cathode was very stable under the H₂O₂ production conditions.

Nitric acid treatment and Ni carbonate catalyst had different effects. The *I*-*E* curve of the Ni₁₀/KB after washing with distilled water cathode (Fig. S5(c)[†]) was overlapped to that of the pristine KB cathode (Fig. S5(a)[†]), and the FE(H₂O₂) of Ni₁₀/KB after washing with water (62%) was almost similar as that of the pristine KB (59%). It is suggested that the Ni₁₀/KB cathode returned to the original KB just by washing with pure water and reversibly due to the removal of the loaded Ni compound. On the other hand, the mechanism of the nitric acid treatment effect was explained by the change of the carbon surface structure, especially by the ratio of sp² and sp³ bonded carbons.^{51,52} The former originated mainly from graphitic and/or aromatic bonded carbon (C=C), and the latter was from aliphatic and/or diamond bonded carbon (C-C). By XPS measurement, the sp²/sp³ ratio of C 1s became higher, and the activity was higher.^{49,53} It was also confirmed that the sp²/sp³ ratio and the peak of the COO functional group at around 289.3 eV in our samples increased after nitric acid treatment

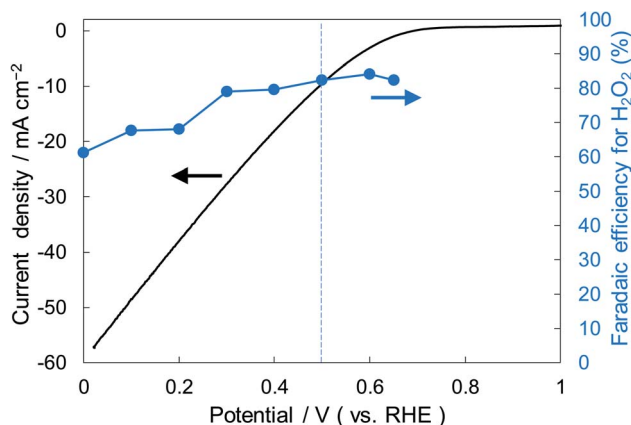


Fig. 6 *I*-*E* curves for Ni₁₀/KB_{HNO₃} (area 1 cm²) at a scan rate of 2 mV s⁻¹ and the FE(H₂O₂) at the passed charge after 5C in terms of the applied potential.

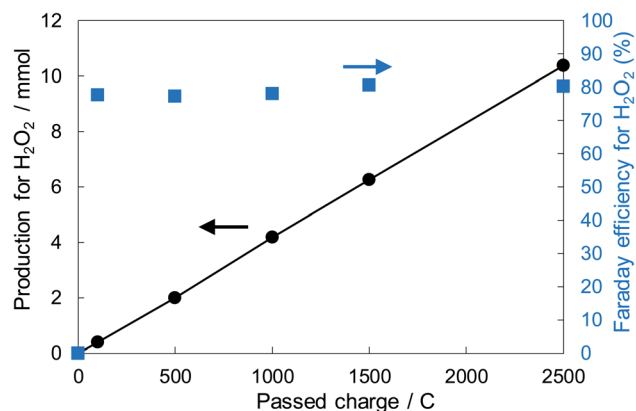


Fig. 7 H₂O₂ production and the FE(H₂O₂) in terms of the passed charge. The cathode used was Ni₁₀/KB_{HNO₃} (loading 1.5 mg cm⁻², 20 cm²). The FE(H₂O₂) was measured at a constant potential of +0.5 V (vs. RHE). The volume of the electrolyte solutions of the anode and cathode chambers was 35 mL.



(Fig. S10†). The increase of sp^2/sp^3 may indicate the increase of the graphitic carbon structure with high conductivity. The C 1s XPS spectrum of KB_{HNO_3} did not change even when the sample was washed with distilled water thoroughly (Fig. S11†), suggesting that the carbon surface structure of the KB powder was irreversibly oxidized or dehydrated by concentrated nitric acid treatment at 353 K.

The positive effect of nitric acid treatment was not observed when the immersed time was short (<1 h), and/or the temperature was low at around room temperature. In the case of KB_{HNO_3} and Ni_{10}/KB_{HNO_3} , the XPS spectra of C 1s were hardly changed by Ni carbonate loading (Fig. S10(c and d)†). From the results, it was concluded that the mechanism of effect by Ni carbonate catalyst was different from that by nitric acid treatment. It was surmised that the presence of small particles of insoluble Ni carbonate catalyst (mainly $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$) on the carbon surface of both KB and KB_{HNO_3} could accelerate the two-electron process from O_2 to H_2O_2 effectively. The detailed mechanism of the nickel carbonate basic hydrate effect is under investigations.

The property of H_2O_2 production on the $BiVO_4/WO_3$ photoanode is known to be highly excellent, and we also confirmed that the $FE(H_2O_2)$ was around 90% initially on our $BiVO_4/WO_3$ photoanode in $KHCO_3$ aqueous solution.^{19,29,32} Finally, the combination of the Ni_{10}/KB_{HNO_3} cathode with the $BiVO_4/WO_3$ photoanode was investigated in the one-compartment cell without any membrane between electrodes in 2.0 M $KHCO_3$ aqueous solution under the solar simulator AM 1.5G (1 SUN). Fig. 8 shows the current–time dependence under simulated solar light irradiation in the two-electrode system without an applied bias potential. The current was not observed between electrodes in the dark condition. When the simulated solar light was irradiated to the photoanode, a photocurrent of >1.75 mA cm^{-2} was observed initially, and the photocurrent was maintained at around 1.5 mA cm^{-2} . This photocurrent value was in agreement with that in the I – E curve at 0 V of the potential (Fig. S12†). The average $FE(H_2O_2)$ from both electrodes was calculated to be 168% in total at passed charge after 0.5C using eqn (5), and the production rate of H_2O_2 was estimated to be 0.92 $\mu mol min^{-1} cm^{-2}$. The values of the apparent solar-to-

chemical energy conversion efficiency for the H_2O_2 production ($STC_{H_2O_2}$) were estimated to be 1.75% without applying an external bias, using eqn (8). This value is, to the best of our knowledge, the highest among all the reported values for H_2O_2 production systems using simulated solar light (Table S3†). We successfully achieved highly efficient H_2O_2 production by only using electrolytes, oxygen, and simulated solar light, without using external electricity, a membrane, and a noble metal.

Conclusion

We have successfully prepared a highly active non-noble-metal electrocatalyst for H_2O_2 production from O_2 in 2.0 M $KHCO_3$ aqueous solution using an *in situ* preparation process. The small particles (10–40 nm) of Ni carbonate prepared by immersion of Ni nitrate in a $KHCO_3$ solution are remarkably effective on the HNO_3 pretreated KB electrode. The highest values of the $FE(H_2O_2)$ and $J_{ap}(H_2O_2)$ of 82% and -9.8 mA cm^{-2} , respectively, were obtained using a Ni_{10}/KB_{HNO_3} cathode at +0.5 V vs. RHE. The cathode is very stable, and the H_2O_2 accumulation concentration can reach 1.0 wt%. Finally, the H_2O_2 production on a $BiVO_4/WO_3$ photoanode and a Ni_{10}/KB_{HNO_3} cathode in a one-compartment photochemical cell was demonstrated without applying an external bias, and the apparent $FE(H_2O_2)$ was 168% in total. The production rate of H_2O_2 was 0.92 $\mu mol min^{-1} cm^{-2}$. The value of $STC_{H_2O_2}$ was estimated to be 1.75% without applying an external bias. This H_2O_2 production system on both electrodes without external bias has great economic advantages compared to a system using a one-side electrode with bias. This one-compartment cell system without any membrane is very simple, and it will be developed using photocatalyst sheets as both cathode and anode electrodes for a large area application.¹⁹ In order to accumulate the produced H_2O_2 further in this system, the development of the suppression method about the H_2O_2 successive decomposition on the photoanode is very important.²⁰ Moreover, the elucidation on the mechanism of the nickel carbonate basic hydrate at the atomic level by computational chemistry is also needed. They are under investigations.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

The present work was partially supported by the International Joint Research Program for Innovative Energy Technology and JSPS KAKENHI Grant Number JP17H06436. The work at BNL was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, & Bioscience, under contract DE-SC0012704.

References

- Z. Qiang, J. H. Chang and C. P. Huang, *Water Res.*, 2002, **36**, 85–94.

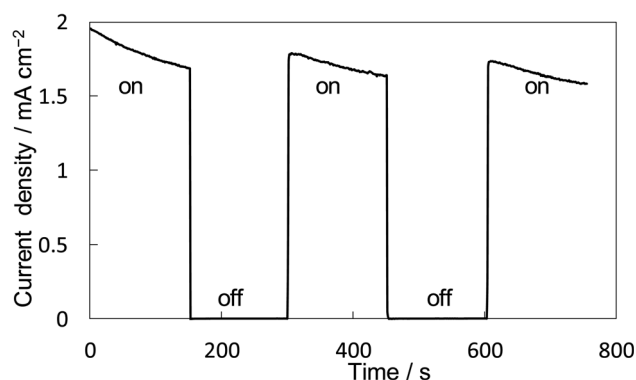


Fig. 8 I – T curve for the $BiVO_4/WO_3$ anode and Ni_{10}/KB_{HNO_3} cathode without applying an external bias under illumination (AM 1.5G, 1 SUN) and dark. Measurement conditions: a two-electrode system into a one-compartment cell was used with 2.0 M $KHCO_3$ aqueous solution under CO_2 and O_2 bubbling each for 50 mL min^{-1} .



- 2 J. M. Campos-Martin, G. Blanco-Brieva and J. L. G. Fierro, *Angew. Chem., Int. Ed.*, 2006, **45**, 6962–6984.
- 3 E. Brillas, I. Sirés and M. A. Oturan, *Chem. Rev.*, 2009, **109**, 6570–6631.
- 4 P. V. Nidheesh and R. Gandhimathi, *Desalination*, 2012, **299**, 1–15.
- 5 M. H. M. T. Assumpção, R. F. B. DeSouza, R. M. Reis, R. S. Rocha, J. R. Steter, P. Hammer, I. Gaubeur, M. L. Calegaro, M. R. V. Lanza and M. C. Santos, *Appl. Catal., B*, 2013, **142–143**, 479–486.
- 6 R. R. Adžić, Recent advances in the kinetics of oxygen reduction, *Electrocatalysis*, 1996, **1**.
- 7 K. Kinoshita, *Electrochemical oxygen technology*, 1992, pp. 193–344.
- 8 B. Šljukić, C. E. Banks and R. G. Compton, *J. Iran. Chem. Soc.*, 2005, **2**, 1–25.
- 9 F. Sandelin, P. Oinas, T. Salmi, J. Paloniemi and H. Haario, *Ind. Eng. Chem. Res.*, 2006, **45**, 986–992.
- 10 J. K. Edwards, E. Ntainjua, A. F. Carley, A. A. Herzing, C. J. Kiely and G. J. Hutchings, *Angew. Chem., Int. Ed.*, 2009, **48**, 8512–8515.
- 11 S. J. Freakley, Q. He, J. H. Harrhy, L. Lu, D. A. Crole, D. J. Morgan, E. N. Ntainjua, J. K. Edwards, A. F. Carley, A. Y. Borisevich, C. J. Kiely and G. J. Hutchings, *Science*, 2016, **351**, 965–968.
- 12 Y. Nomura, T. Ishihara, Y. Hata, K. Kitawaki, K. Kaneko and H. Matsumoto, *ChemSusChem*, 2008, **1**(7), 619–621.
- 13 F. Li, Q. Shao, M. Hu, Y. Chen and X. Huang, *ACS Catal.*, 2018, **8**, 3418–3423.
- 14 I. Yamanaka, T. Onizawa, S. Takenaka and K. Otsuka, *Angew. Chem., Int. Ed.*, 2003, **42**, 3653–3655.
- 15 I. Yamanaka and T. Murayama, *Angew. Chem., Int. Ed.*, 2008, **47**, 1900–1902.
- 16 T. Iwasaki, Y. Masuda, H. Ogihara and I. Yamanaka, *Electrocatalysis*, 2018, **9**(2), 236–242.
- 17 W. T. Li, A. Bonakdarpour, E. Gyenge and D. P. Wilkinson, *J. Appl. Electrochem.*, 2018, **48**, 985–993.
- 18 C. Xia, Y. Xia, P. Zhu, L. Fan and H. Wang, *Science*, 2019, **366**(6462), 226–232.
- 19 K. Fuku, Y. Miyase, Y. Miseki, T. Funaki, T. Gunji and K. Sayama, *Chem.–Asian J.*, 2017, **12**, 1111–1119.
- 20 Y. Miyase, S. Takasugi, S. Iguchi, Y. Miseki, T. Funaki, T. Gunji, K. Sasaki, E. Fujita and K. Sayama, *Sustainable Energy Fuels*, 2018, **2**, 1621–1629.
- 21 T. H. Jeon, H. Kim, H. Kim and W. Choi, *Energy Environ. Sci.*, 2020, **13**, 1730–1742.
- 22 X. Shi, Y. Zhang, S. Siahrostami and X. L. Zheng, *Adv. Energy Mater.*, 2018, **8**, 1801158.
- 23 Y. Liu, X. Quan, X. Fan, H. Wang and S. Chen, *Angew. Chem., Int. Ed.*, 2015, **54**, 6837–6841.
- 24 C. Zhao, B. Li and Q. Zhang, *J. Energy Chem.*, 2019, **34**, 10–11.
- 25 Z. Chen, S. Chen, S. Siahrostami, P. Chakthranont, C. Hahn, D. Nordlund, S. Dimosthenis, J. K. Nørskov, Z. Bao and T. F. Jaramillo, *React. Chem. Eng.*, 2017, **2**, 239–245.
- 26 R. A. Sidik, A. B. Anderson, N. P. Subramanian, S. P. Kumaraguru and B. N. Popov, *J. Phys. Chem. B*, 2006, **110**, 1787–1793.
- 27 Y. H. Lee, F. Li, K. -H. Chang, C. C. Hu and T. Ohsaka, *Appl. Catal., B*, 2012, **126**, 208–214.
- 28 K. Zhao, Y. Su, X. Quan, Y. Liu, S. Chen and H. Yu, *J. Catal.*, 2018, **357**, 118–126.
- 29 F. Yu, M. Zhou and X. Yu, *Electrochim. Acta*, 2015, **163**, 182–189.
- 30 S. Fukuzumi and Y. Lee, *Chem. Eur. J.*, 2018, **24**, 5016–5031.
- 31 K. Ueno and H. Misawa, *NPG Asia Mater.*, 2013, **5**, e61.
- 32 K. Fuku, Y. Miyase, Y. Miseki, T. Gunji and K. Sayama, *RSC Adv.*, 2017, **7**, 47619–47623.
- 33 X. Shi, S. Siahrostami, G. Li, Y. Zhang, P. Chakthranont, F. Studt, T. Jaramillo, X. L. Zheng and J. Nørskov, *Nat. Commun.*, 2017, **8**, 701.
- 34 J. Liu, Y. Zou, B. Jin, K. Zhang and J. H. Park, *ACS Energy Lett.*, 2019, **4**, 3018–3027.
- 35 K. Zhang, J. Liu, L. Wang, B. Jin, X. Yang, S. Zhang and J. H. Park, *J. Am. Chem. Soc.*, 2020, **142**, 8641–8648.
- 36 Y. Xue, Y. Wang, Z. Pan and K. Sayama, *Angew. Chem., Int. Ed.*, 2021, **60**, DOI: 10.1002/anie.202011215.
- 37 J. H. Kim, J. Jang, Y. H. Jo, F. F. Abdi, Y. H. Lee, R. v. d. Krol and J. S. Lee, *Nat. Commun.*, 2016, 13380.
- 38 Z. Lu, G. Chen, S. Siahrostami, Z. Chen, K. Liu, J. Xie, L. Liao, T. Wu, D. Lin, Y. Liu, T. F. Jaramillo, J. K. Nørskov and Y. Cui, *Nat. Catal.*, 2018, **1**, 156–162.
- 39 Z. Chen, S. Chen, S. Siahrostami, P. Chakthranont, C. Hahn, D. Nordlund, S. Dimosthenis, J. K. Nørskov, Z. Bao and T. F. Jaramillo, *React. Chem. Eng.*, 2017, **2**, 239–245.
- 40 N. Jia, Y. Liu, L. Wang, P. Chen, X. Chen, Z. An and Y. Chen, *ACS Sustainable Chem. Eng.*, 2020, **8**, 2883–2891.
- 41 W. Zhou, X. Meng, J. Gao and A. N. Alshawabkeh, *Chemosphere*, 2019, **225**, 588–607.
- 42 J. Lee, G. Su Park, H. Il Lee, S. T. Kim, R. Cao, M. Liu and J. Cho, *Nano Lett.*, 2011, **11**, 5362–5366.
- 43 J. Li, N. Zhou, J. Song, L. Fu, J. Yan, Y. Tang and H. Wang, *ACS Sustainable Chem. Eng.*, 2018, **6**, 413–421.
- 44 T. Kinumoto, J. Nakamura, K. Kikuchi and Z. Ogumi, *Tanso*, 2010, **244**, 133–136.
- 45 K. Fuku and K. Sayama, *Chem. Commun.*, 2016, **52**, 5406–5409.
- 46 D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm, *Tables for the First Thirty-Four Elements in the Standard Order of Arrangement*, U. S. Government Printing Office, 1968.
- 47 S. Maeno, *Tanso*, 2006, **222**, 140–146.
- 48 R. Grauer, *Solubility Products of M(II)-Carbonates*, PSI Bericht Nr. 99-04, 1999.
- 49 A. Moraes, M. H. M. T. Assumpção, F. C. Simões, V. S. Antonin, M. R. V. Lanza, P. Hammer and M. C. Santos, *Electrocatalysis*, 2016, **7**, 60–69.
- 50 I. Yamanaka and T. Murayama, *Angew. Chem., Int. Ed.*, 2008, **47**, 1900–1902.
- 51 R. Haerle, E. Riedo, A. Pasquarello and A. Baldereschi, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **65**, 045101.
- 52 J. C. Lascovich, R. Giorgi and S. Scaglione, *Appl. Surf. Sci.*, 1991, **47**, 17–21.
- 53 R. Pandiyan, N. Deegan, A. Dirany, P. Drogui and M. A. El Khakani, *Carbon*, 2015, **94**, 988–995.

