

Effects of chloride and other anions on electrochemical chlorine evolution over self-doped TiO₂ nanotube array

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Abstract—Electrochemically reduced TiO₂ nanotube arrays (r-TiO₂ NTA) have emerged as an alternative that can replace the dimensionally stable anode (DSA[®]) due to comparable performance for chlorine evolution reaction (CIER). However, previous studies have reported applications of r-TiO₂ NTA for CIER only under limited conditions (concentrated NaCl solution without other anions). Thus, the potential of r-TiO₂ NTA for CIER has not yet been fully demonstrated. Therefore, this study focused on investigating CIER of r-TiO₂ NTA under various parameters such as chloride concentration (5-1,000 mM) and the presence of other anions (i.e., SO₄²⁻, HPO₄²⁻, and CO₃²⁻). The results suggest that, at low chloride concentration (5-50 mM NaCl), the r-TiO₂ NTA exhibited higher performance for CIER (production rate of 3.35-9.82 mg l⁻¹ min⁻¹, current efficiency of 14.43-42.04%, energy consumption of 69.24-11.02 Wh g(Cl₂)⁻¹) than RuO₂ (2.55-7.88 mg l⁻¹ min⁻¹, 11.07-33.85% and 77.29-6.84 Wh g(Cl₂)⁻¹, respectively). Additionally, other anions did not affect the CIER of r-TiO₂ NTA more than RuO₂. These can be explained by the indirect pathway of CIER in r-TiO₂ NTA while the direct pathway of RuO₂ was negatively affected by dilute chloride and other anions.

Keywords: Reduced TiO₂ Nanotube Array, Electrochemical Self-doping, Chlorine Evolution, Chloride Concentration, Anion Effect, Hydroxyl Radical

INTRODUCTION

The electrochemical oxidation process (EOP) has been extensively studied in the water treatment field due to its various advantages such as ease of operation, lack of requirement of additional chemicals, and high effectiveness for the production of various oxidants during the electrolysis of water [1,2]. Chlorine is a well-known fundamental oxidant produced by EOP that has been utilized for the degradation of organic pollutants and disinfection of water [3-5]. Several operational parameters such as electrode materials, operational modes regarding the application of current and voltage, and feed conditions (i.e., pH, composition and temperature) govern the efficiency of oxidant production via EOP [6]. Among them, anode materials are primarily responsible for the production of oxidants in high yield [3]. The dimensionally stable anode (DSA[®]) is a commercially available anode that has been widely used for the effective production of chlorine [7-9].

TiO₂ nanotube array (TiO₂ NTA) has garnered considerable attention as a promising anode material for EOP because it has numerous beneficial properties such as highly aligned open pore

nanostructure, large surface area, and chemical stability [10,11]. In addition, it can be easily fabricated via electrochemical anodization, and a well-organized nanostructure can be established onto a titanium substrate without requiring additional processes for TiO₂ [12-14]. The facile fabrication of the TiO₂ NTA allows them to be employed for various applications. Despite these advantages, they have been limited to applications as an anode material for oxidant production because they are semi-conductive and thus exhibit low electrocatalytic activity [15]. To overcome this, various approaches such as thermal hydrogenation and incorporation of metal and non-metal impurities have been proposed [16-20].

Electrochemical self-doping is another method to enhance the electrocatalytic activity of the TiO₂ NTA. This process involves forming reduced TiO₂ NTA (r-TiO₂ NTA) by electrochemical reduction possibly leading to trivalent titanium as self-dopant. The electrochemical reduction of anatase TiO₂ NTA (a-TiO₂ NTA) converts the surface a-TiO₂ NTA from gray to blue. It is attributed to the significantly improved dopant level of r-TiO₂ NTA via electrochemical reduction compared to a-TiO₂ NTA [21]. Unlike the process of impurity incorporation, the electrochemical self-doping process imparts high structural stability to the TiO₂ NTA because of the formation of Ti³⁺ that causes a small distortion in the crystal structure and surface morphology of the TiO₂ NTA [22]. After doping, the r-TiO₂ NTAs exhibited significantly improved capacitive and

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electrocatalytic activity for the chlorine evolution reaction (ClER); their performance was comparable to that of the commercially available DSA[®] [23-26]. Therefore, there have been many studies with r-TiO₂ NTA for environmental applications (e.g., energy storage device, wastewater treatment, disinfection and desalination) [27-31].

However, the chlorine evolution performance on r-TiO₂ NTA has been demonstrated in limited experimental conditions with highly concentrated NaCl solution (i.e., high concentration of chloride (Cl⁻) ions as a precursor for electro-generated chlorine (Cl₂), 2Cl⁻ → Cl₂ + 2e⁻, E₀ = 1.36 V vs NHE). Thus, the r-TiO₂ NTA was not utilized in practical environmental and industrial applications. Consequently, in order to expand its application spectrum, the performance of the ClER over the r-TiO₂ NTA at low Cl⁻ concentration and in the presence of other anions needs to be investigated. This will facilitate the application of the TiO₂ NTA for the treatment of tap water, ground water, and wastewater. Therefore, it is necessary to assess the features of the ClER over r-TiO₂ NTA under various conditions to verify their applicability as an anode for EOP.

In this study, we attempted to verify the potential of r-TiO₂ NTA for the ClER at various Cl⁻ concentrations ranging from 5 to 1,000 mM and in presence of other anions (e.g., SO₄²⁻, HPO₄²⁻, and CO₃²⁻). The electrocatalytic property of r-TiO₂ NTA was compared to that of RuO₂, which was one of the representatives for DSA[®]. In addition, the advantages of r-TiO₂ NTA for ClER in the conditions were elucidated by revealing its indirect mechanism for ClER with *t*-BuOH.

EXPERIMENTAL SECTION

1. Fabrication of Electrodes

The r-TiO₂ NTA was synthesized via the electrochemical self-doping of the anodized TiO₂ NTAs (anatase) by following previously reported procedures [23-26]. In brief, the TiO₂ NTA were prepared by anodization in 30 mL electrolyte containing H₂O (2.5 wt%), NH₄F (0.2 wt%), and ethylene glycol (97.3 wt%) at a constant voltage of 40 V for 5 h. Titanium foil (1 cm × 2 cm) and platinum mesh were selected as the anode and cathode, respectively. The synthesized TiO₂ NTA were completely purified using deionized water (DI), followed by a thermal treatment at 450 °C for 1 h under atmospheric conditions. The electrochemical self-doping of the thermally treated TiO₂ NTA (anatase; a-TiO₂ NTA) was performed in a phosphate buffer solution (PBS; 0.1 M KH₂PO₄ with NaOH, pH 7.2) and -16.7 mA cm⁻² for 90 sec. The RuO₂ electrocatalyst was prepared by dropping 50 μl of the ruthenium precursor (RuCl₃·H₂O 0.2 M (HCl:DI=1:1) on a titanium plate that was treated with 1 M HCl at 80 °C for 30 min, followed by annealing at 450 °C for 1 h.

2. Surface and Electrochemical Properties

The morphology of the r-TiO₂ NTAs was examined by scanning electron microscopy (SEM; JSM-6700F, JEOL, Japan). X-ray diffraction (XRD) analysis (Bruker D8 DISCOVER, Germany) was conducted to characterize the material of r-TiO₂ NTA. The electrochemical property of the r-TiO₂ NTAs was investigated through staircase linear sweep voltammetry (SLSV) (PARSTAT 2273A, Princ-

eton Applied Research, U.S.A.).

The level of dopant (charge carrier density) of a-TiO₂ and r-TiO₂ NTA was estimated with Mott-Schottky plot (Eq. (1)), which was obtained via EIS measurements of the complex capacitance at AC potential of 10 mV and DC potential of open circuit potential in 0.1 M phosphate buffer solution (PBS).

$$\frac{1}{C_{sc}^2} = \left(\frac{2}{e \epsilon_0 \epsilon N_D} \right) (E_{app} - E_{fb} - \frac{kT}{e}) \quad (1)$$

where C_{sc}⁻² is the space charge capacitance (F⁻²·cm⁴), E_{app} and E_{fb} indicate an applied potential and flat band potential, respectively. N_D is the donor density (cm⁻³) and e is the electronic charge. ε is the dielectric constant of TiO₂ (ε(TiO₂)=31 for anatase, Ref. of [20]) and ε₀ is the permittivity of the free space. k is the Boltzmann constant and T is the operational temperature.

To understand the ClER on r-TiO₂ NTA, the ohmic drop was corrected with Eq. (2) and (3) as below [25,32].

$$\frac{\Delta \eta}{\Delta i} = \frac{b}{i} + R \quad (2)$$

$$\eta_{corr} = \eta - iR \quad (3)$$

where η, i, b, and R represent the overpotential, current in the SLSV, Tafel slope (V dec⁻¹), and total area of uncompensated resistance (Ω cm²), respectively.

3. Evolution of Chlorine and other Oxidants

Cl₂ was electrochemically produced in an undivided electrocatalytic cell (30 ml) with various NaCl concentration ranging from 5 to 1,000 mM in the absence and the presence of sodium salts of the following anions: HPO₄²⁻, SO₄²⁻, and CO₃²⁻ (Sigma Aldrich Co.). The Cl₂ and other oxidant concentration (mg l⁻¹ as total Cl₂) was quantitatively measured by the *N,N*-diethyl-*p*-phenylenediamine (DPD) colorimetric method using a spectrophotometer (DR/900, HACH Co., Loveland, USA) at 530 nm [3]. To examine the effect of anions, each anion was electrolyzed in the absence of Cl⁻ and the capability of generated oxidants was measured with the same DPD which has potassium iodide (KI). The ionic strength of the electrolyte was maintained by using NaClO₄ as a supporter solution in the same amount as the 1,000 mM NaCl solution.

The mechanism of ClER over the TiO₂ NTAs and RuO₂ was elucidated by following the terephthalic acid (TA; 0.1 mM) degradation on each electrode using high-performance liquid chromatography (HPLC; YL9100, Younglin Co., Korea) performed in a methanol and formic acid (0.1%) mixture (v/v, 60:40) [33]. The effect of hydroxyl radicals (·OH) on the ClER was examined by adding 0.03-1 M *t*-BuOH and by conducting a scavenging test during chlorine production [23].

The current efficiency and energy consumption for generation chlorine were calculated by Eqs. (4) and (5), respectively.

$$\text{Current efficiency (\%)} = \frac{nFCV}{itM_{Cl_2}} \quad (4)$$

$$\text{Energy consumption (Wh} \cdot \text{g}^{-1}) = \frac{i \int \text{edt}}{CV} \quad (5)$$

where C is the concentration of electro-generated chlorine (g l⁻¹), V is the volume of electrolyte (l), n is the number of electrons (1

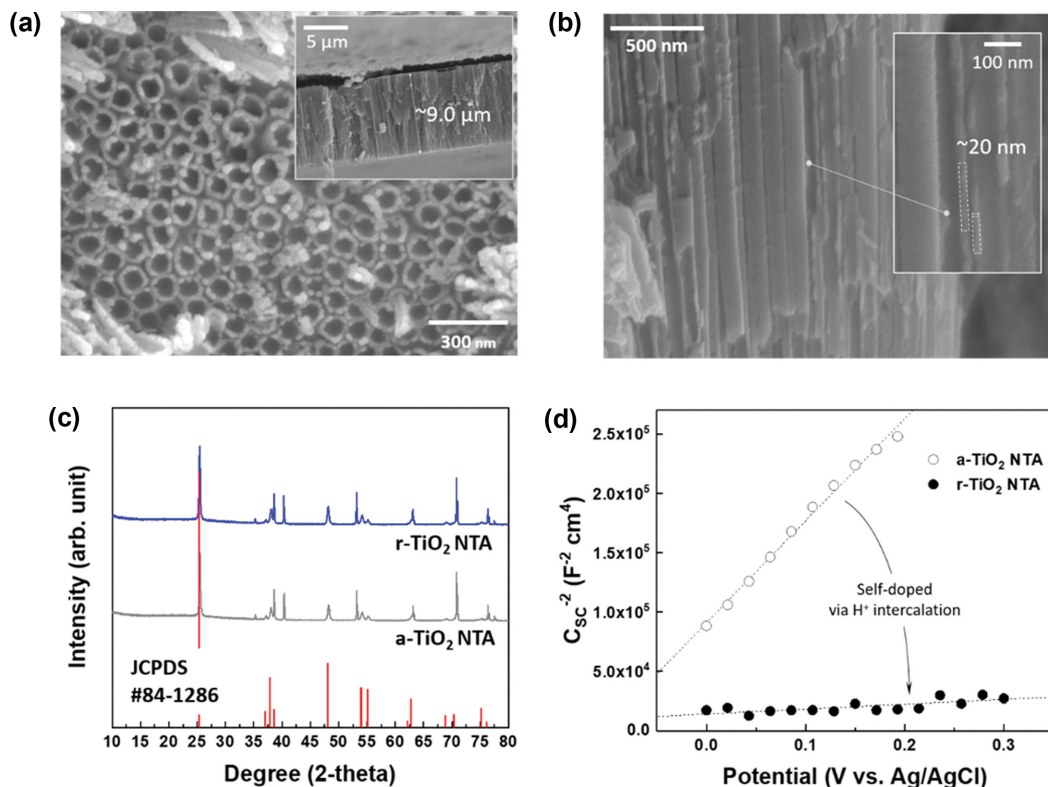


Fig. 1. Surface morphology and characteristics of the reduced TiO_2 nanotube array (r-TiO_2 NTA): (a) top and (b) cross-sectional views of the scanning electron microscopies (SEM), (c) X-ray diffraction (XRD) patterns, and (d) Mott-Schottky plot of r-TiO_2 NTA; The inset of panel A indicates the thickness of r-TiO_2 NTA and the XRD patterns of the anatase TiO_2 NTA (a-TiO_2 NTA) were indexed with reference to the JCPDS file (PDF 84-1286). The Mott-Schottky plot was obtained with AC potential of 10 mV (frequency=100 Hz) and DC potential of open circuit potential in 0.1 M KH_2PO_4 with NaOH (pH of 7.2).

eq mol^{-1}), F is the Faradaic constant ($96,485 \text{ C eq}^{-1}$), M_{Cl_2} is the molecular weight of chlorine (71 g mol^{-1}), i is applied current (A) and t is the electrolysis time (s), and e is the operational cell voltage (V).

RESULTS AND DISCUSSION

Fig. 1 shows the surface morphology and doping level of the prepared r-TiO_2 NTA as examined by the SEM images ((a) and (b)), XRD patterns (c), and Mott-Schottky plots (d) of the sample. As shown in Fig. 1(a) and (b), the r-TiO_2 NTA have a well-organized nanostructure with a pore size, wall thickness, and tube length of approximately $111.5 (\pm 16.6) \text{ nm}$, 20 nm , and $9.0 \mu\text{m}$, respectively. The XRD pattern (Fig. 1(c)) shows that the peak positions of the r-TiO_2 NTAs are consistent with those of the a-TiO_2 NTA (JCPDS, PDF 84-1286), implying that electrochemical self-doping has a negligible effect on the structural property of the r-TiO_2 NTA. However, a significant improvement in the doping level was observed in the r-TiO_2 NTA (Fig. 1(d)). The slope of the Mott-Schottky plot for the r-TiO_2 NTA was much smaller than that of the pristine a-TiO_2 NTA, indicating a high doping level of the r-TiO_2 NTA. These findings are in accordance with previous studies [21], and accordingly we can confirm that the r-TiO_2 NTA was well synthesized.

The electrocatalytic activity of the r-TiO_2 NTAs and RuO_2 for the

CIER was examined by investigating the concentration (mg l^{-1}) of electro-generated chlorine, its production rate ($\text{mg l}^{-1} \text{ min}^{-1}$), charge efficiency (%), and energy consumption (Wh g^{-1}). The results of the analyses are presented in Fig. 2. Fig. 2(a) shows a linear correlation between the chlorine produced over the r-TiO_2 NTA and RuO_2 and the electrolysis time at various Cl^- concentrations. Clearly, increasing the NaCl concentration improved the production of Cl_2 in all samples. However, the r-TiO_2 NTA and RuO_2 displayed different chlorine evolution rates at different NaCl concentration (Fig. 2(b)). At low Cl^- concentration (5-50 mM NaCl), the r-TiO_2 NTA exhibit higher production efficiency with a Cl_2 generation rate of $3.35\text{-}9.82 \text{ mg l}^{-1} \text{ min}^{-1}$, current efficiency of 14.43-42.04%, and energy consumption of $69.24\text{-}11.02 \text{ Wh g}(\text{Cl}_2)^{-1}$ than RuO_2 did (generation rate of $2.55\text{-}7.88 \text{ mg l}^{-1} \text{ min}^{-1}$, current efficiency of 11.07-33.85%, and energy consumption of $77.29\text{-}6.84 \text{ Wh g}(\text{Cl}_2)^{-1}$). In contrast, at higher Cl^- concentration (100-1,000 mM NaCl), RuO_2 shows higher performance for the CIER. In particular, at 1,000 mM NaCl, the current efficiency of RuO_2 (~76%) is considerably higher than that of the r-TiO_2 NTA (64.83%). Thus, at low NaCl concentrations the CIER is favored over the r-TiO_2 NTA, whereas at higher concentrations it is favored over RuO_2 . These results can be explained by the different mechanisms of the CIER on the r-TiO_2 NTA and RuO_2 . To better understand the mechanism, the formation of $\cdot\text{OH}$ was examined.

As shown in Fig. 3, the effect of $\cdot\text{OH}$ on the CIER over the r-TiO_2

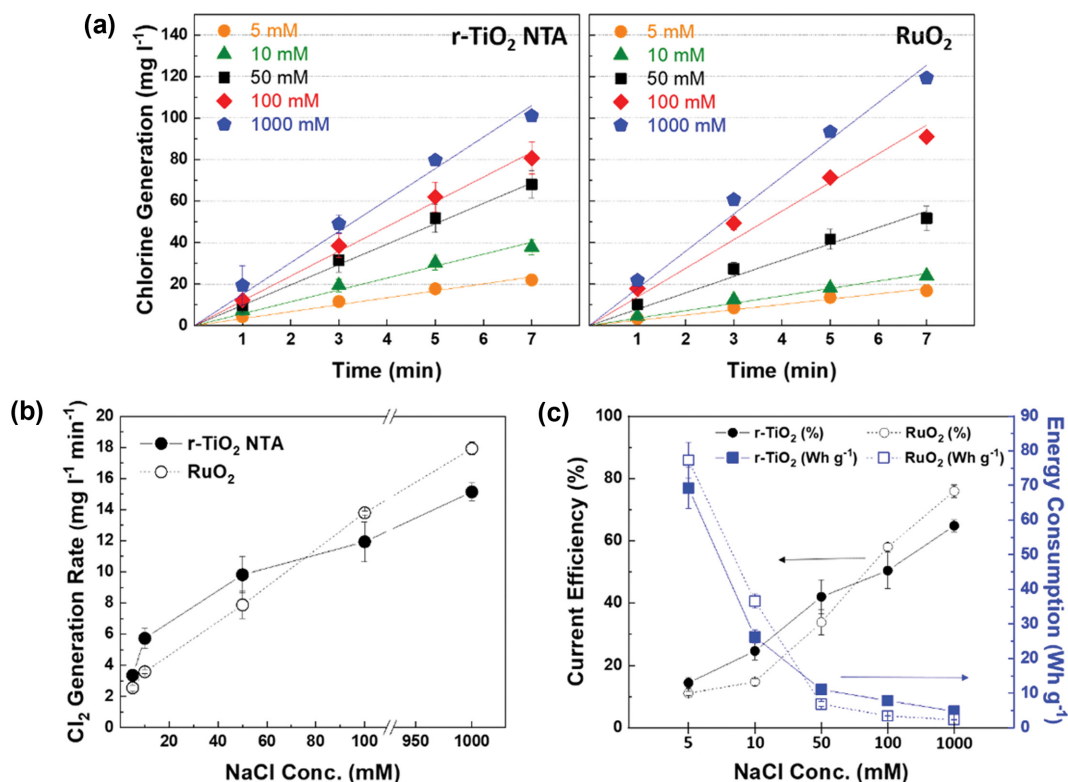


Fig. 2. Chlorine (Cl₂) evolution performance on r-TiO₂ NTA and RuO₂: (a) Cl₂ concentration, (b) Cl₂ evolution rate, and (c) current efficiency and energy consumption. The Cl₂ evolution was examined at a constant current of 16.7 mA cm⁻² for various NaCl concentrations ranging from 5, 10, 50, 100, and 1,000 mM.

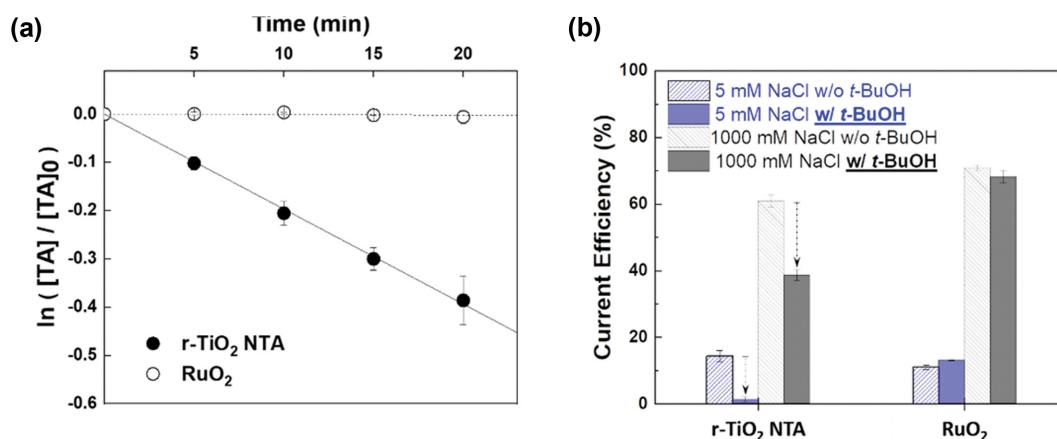


Fig. 3. (a) Production of hydroxyl radical examined by semi-log plot with 0.1 mM terephthalic acid solution as a hydroxyl radical ($\cdot\text{OH}$) probe compound and (b) the effect of $\cdot\text{OH}$ scavenger on chlorine (Cl₂) evolution (current efficiency) of reduced TiO₂ nanotube (r-TiO₂ NTA) and RuO₂; in panel A, the $\cdot\text{OH}$ production was conducted in 0.1 M KH₂PO₄ with NaOH (pH of 7.2) under constant current of 16.7 mA cm⁻² for 20 min. In panel B, the current efficiencies in 5 mM and 1,000 mM NaCl with addition of 0.03-1 M *t*-BuOH under applying constant current of 16.7 mA cm⁻² for 5 min were presented.

NTAs and RuO₂ was investigated by examining the steady-state production rate of $\cdot\text{OH}$, which was determined by the degradation of an $\cdot\text{OH}$ probe compound (terephthalic acid, 0.1 mM) and the CIER in presence of an excess $\cdot\text{OH}$ scavenger (*t*-BuOH of 0.03-1 M). The $\cdot\text{OH}$ production over the r-TiO₂ NTAs follows pseudo-first-order kinetics (linear slope in semi-log plot in Fig. 3(a)) [33] and the steady-state rate ($\sim 3.28 \times 10^{-4} \text{ s}^{-1}$) is almost 200-times higher

than that of RuO₂ ($1.67 \times 10^{-6} \text{ s}^{-1}$), indicating the high activity of the r-TiO₂ NTAs for $\cdot\text{OH}$ production. The different behavior for $\cdot\text{OH}$ production indicates that r-TiO₂ NTA and RuO₂ have the different CIER mechanism. In addition, the addition of excess *t*-BuOH, an $\cdot\text{OH}$ scavenger, causes the CIER over the r-TiO₂ NTA to be completely inhibited in 5 mM and 1,000 mM NaCl; however, the CIER over RuO₂ remains largely unaffected (Fig. 3(b)). These findings

suggest that the ClER over the r-TiO₂ NTA is mediated by ·OH indirectly, but that over RuO₂ takes place via the direct oxidation of Cl⁻ ions on the surface [3]. In this regard, in dilute Cl⁻ solutions, wherein the mass transfer of Cl⁻ is limited, ·OH produced over the r-TiO₂ NTAs could oxidize Cl⁻ ions to Cl₂ via diffusion from the anode surface easier than RuO₂. In contrast, in highly concentrated Cl⁻ solutions, the mass transfer limitation of Cl⁻ is negligible; thus, RuO₂ which has the direct pathway for Cl₂ generation is more efficient in ClER than the r-TiO₂ NTA.

The role of ·OH in the ClER on r-TiO₂ NTA and RuO₂ is more clearly demonstrated by the current-overpotential curves measured using the SLSV method (Fig. 4). Note that the curves were adjusted by iR drop compensation to clarify ClER in various Cl⁻ concentration. As shown in Fig. 4, there are two major aspects on ClER of r-TiO₂ NTA and RuO₂. First, small differences in the SLSV curve on r-TiO₂ NTA were found at different Cl⁻ concentration during which RuO₂ exhibited a large dependency with Cl⁻ concentration. This implies that Cl⁻ concentration is a major factor to govern ClER on RuO₂ with direct oxidation. However, the effect

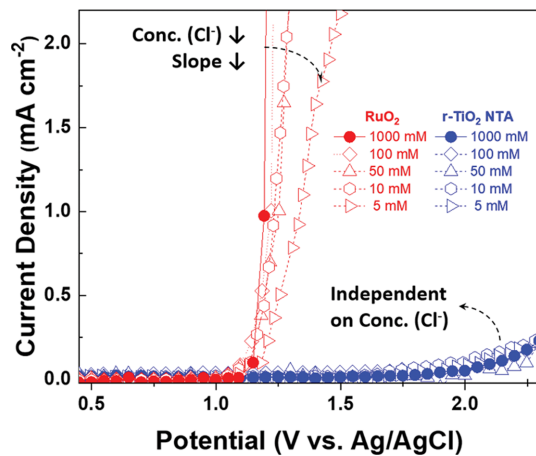


Fig. 4. Current-overpotential curves examined by staircase linear sweep voltammetry (SLSV) measurement of reduced TiO₂ nanotube array (r-TiO₂ NTA) and RuO₂ at various NaCl concentration ranging from 5 mM, 10 mM, 50 mM, 100 mM and 1,000 mM with a step height and step of 1 min (scan rate of 0.83 mV/s).

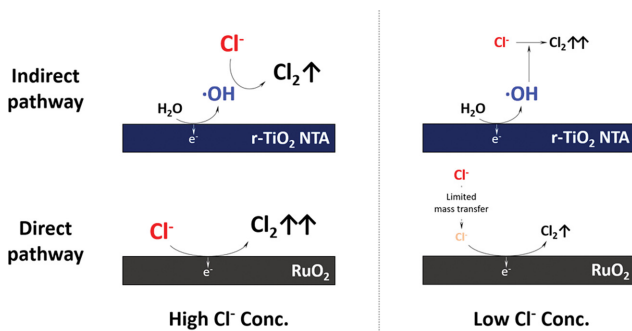


Fig. 5. Schematic illustration for the chlorine evolution mechanisms of r-TiO₂ NTA and RuO₂ in high and low chloride concentrations.

of Cl⁻ concentration on ClER of r-TiO₂ NTA is negligible with the reaction pathway mediated by ·OH. Second, at low Cl⁻ concentration, although the current on r-TiO₂ NTA in SLSV is much less than that of RuO₂, r-TiO₂ NTA led to better ClER performance (Fig. 2) than RuO₂. It can be explained by that the indirect man-

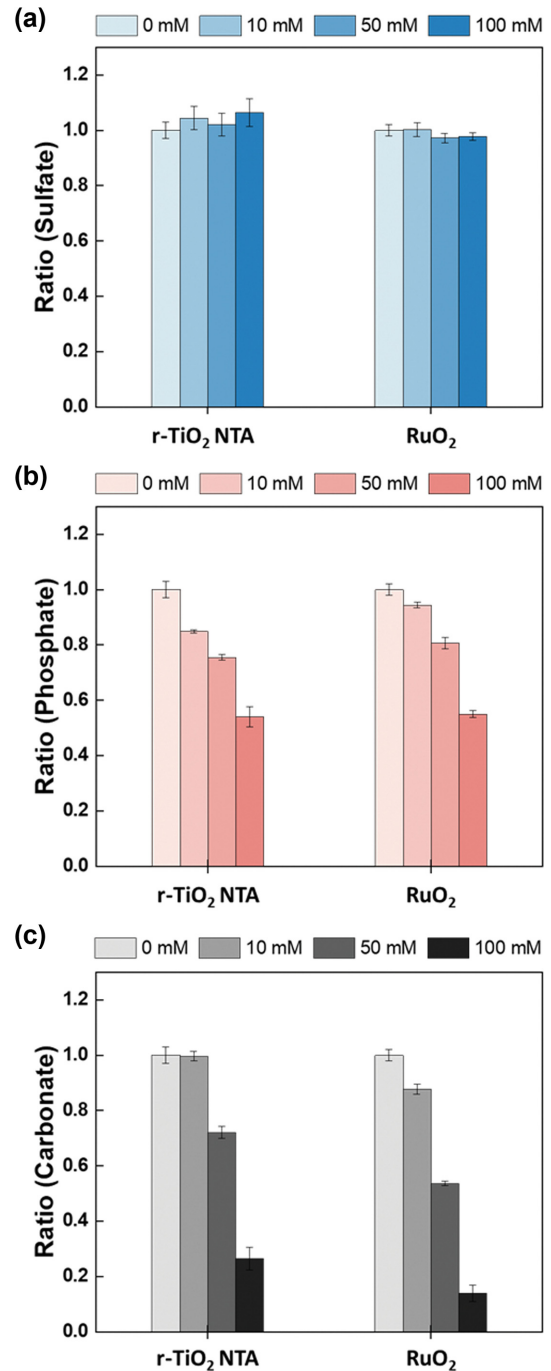


Fig. 6. Effects of anions including (a) SO₄²⁻, (b) HPO₄²⁻ and (c) CO₃²⁻ on chlorine (Cl₂) evolution of reduced TiO₂ nanotube array (r-TiO₂ NTA) and RuO₂. Each generated Cl₂ in various anions was presented as a ratio to the result in the absent of the anions. Cl₂ evolution was conducted with a constant current of 16.7 mA/cm² at 1,000 mM NaCl with concentration of anions ranging from 10 to 100 mM for 7 min.

Table 1. Effects of anions for oxidant (Cl₂) formation in the presence and absence of chloride ion; DPD method, applied current density of 16.7 mA cm⁻², electrolysis time of 7 min, concentration of anions including HPO₄²⁻, SO₄²⁻ and CO₃²⁻ of 50 mM in 1,000 mM NaClO₄ supporter electrolyte. Note that the results in the only Cl⁻ (1,000 mM) condition were from Fig. 2(a)

Unit: mg l ⁻¹ as Cl ₂		Cl ⁻ (Only)	SO ₄ ²⁻	HPO ₄ ²⁻	CO ₃ ²⁻	Supporter (ClO ₄ ⁻)
r-TiO ₂ NTA	w/Cl ⁻	99.33 (±2.89)	101.33 (±4.04)	75.00 (±1.00)	71.67 (±2.08)	-
	w/o Cl ⁻	-	2.25 (±0.08)	0.59 (±0.01)	0.15 (±0.01)	0.04 (±0.00)
RuO ₂	w/Cl ⁻	119.33 (±2.51)	116.00 (±2.00)	96.33 (±2.52)	64.00 (±1.00)	-
	w/o Cl ⁻	-	0.04 (±0.02)	0.03 (±0.01)	0.08 (±0.02)	0.02 (±0.001)

ner of r-TiO₂ NTA in ClER can lead to small effect of mass transfer of Cl⁻ via the diffusion of produced hydroxyl radical from the electrode surface at low Cl⁻ concentration. On the other hand, at high Cl⁻ concentration, small mass transfer limitation of Cl⁻ provide an optimized environment for ClER on both of the electrodes, and thus they can reveal the high ClER performance (refer to Fig. 5).

To further investigate chlorine evolution over the r-TiO₂ NTA, the effect of sulfate (SO₄²⁻), phosphate (HPO₄²⁻), and carbonate (CO₃²⁻) ions on the ClER was examined (Fig. 6). As shown in Fig. 6, the presence of anions caused the ClER over the r-TiO₂ NTA and RuO₂ to be suppressed, and the extent of ClER suppression increased with the anion concentration. The addition of SO₄²⁻, HPO₄²⁻, and CO₃²⁻ ions caused the performance of ClER over RuO₂ to decrease: the production rate (~2.28 mg l⁻¹ min⁻¹) and charge efficiency decreased by ~14% and 9.69%, respectively (Fig. S1 and S2), compared to those obtained in the absence of anions (Fig. 2). However, the effect of anions on the ClER over the r-TiO₂ NTA was relatively less significant than that over RuO₂. Exceptionally, the ClER of r-TiO₂ NTA was improved in the presence of SO₄²⁻. Considering that the ClER of the r-TiO₂ NTA is mediated by ·OH (Fig. 3 and the detailed mechanism provided in previous studies [23,24,28]), it is plausible that reaction of ·OH and Cl⁻ ions is interfered in the presence of anions.

This can be well supported by the produced oxidants (Table 1). From the results in Table 1, the production of unspecified oxidants from the anions was confirmed by electrolysis with r-TiO₂ NTA in each anion, not including Cl⁻ ions. It is assumed that P₂O₈⁴⁻, S₂O₈²⁻, and C₂O₆²⁻ were formed by the reaction between ·OH and the anions [31,34]. The oxidants formed on r-TiO₂ NTA were considerably higher than RuO₂. Interestingly, the presence of SO₄²⁻ resulted in higher yield of oxidants (~2.25 mg l⁻¹ as Cl₂) compared to the HPO₄²⁻ and CO₃²⁻ (~0.59 mg l⁻¹ as Cl₂ and ~0.15 mg l⁻¹ as Cl₂, respectively). This indicates that SO₄²⁻ is more favorable for the reaction of ·OH, which can be a cause for the enhanced ClER of the r-TiO₂ NTA in the presence of SO₄²⁻.

CONCLUSION

We evaluated the chlorine evolution on r-TiO₂ NTA under various experimental conditions including different NaCl concentrations and presence of interfering anions. The mechanism of ClER on the r-TiO₂ NTA was verified with a scavenging test of ·OH. As major results, first, r-TiO₂ NTA revealed better Cl₂ evolution performance than RuO₂ at low NaCl concentration ranging from 5-100 mM, while highly improved ClER performance on RuO₂ was

found at high NaCl concentration (1,000 mM) compared to r-TiO₂ NTA. Second, in the presence of anions (i.e., SO₄²⁻, HPO₄²⁻ and CO₃²⁻), the ClER of r-TiO₂ NTA was slightly less suppressed than RuO₂. Considering the ClER mechanism of r-TiO₂ NTA mediated by ·OH, it is attributed to that the additional oxidants formed by the reaction of anions with ·OH leading to increase oxidant efficacy of ClER. This suggests the ·OH plays an important role in ClER of r-TiO₂ NTA. These results can provide a better understating the properties of r-TiO₂ NTA as an anode for ClER and open various opportunities for implantation of r-TiO₂ NTA in environmental and industrial applications. Additionally, with these results, it would lead to the further success of r-TiO₂ NTA to improve the stability of r-TiO₂ NTA for oxidation reactions.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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Supporting Information

Effects of chloride and other anions on electrochemical chlorine evolution over self-doped TiO₂ nanotube array

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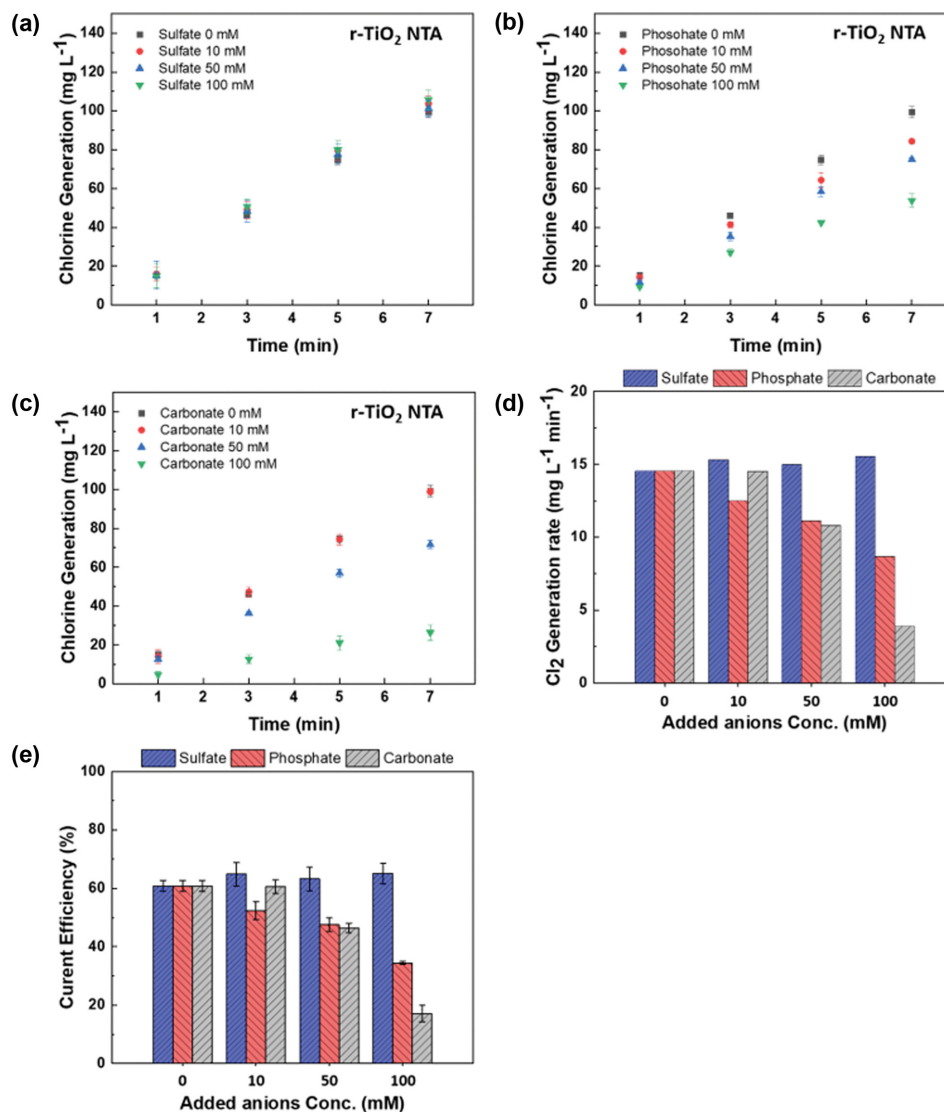


Fig. S1. Chlorine (Cl₂) evolution performance on r-TiO₂ NTA in various anions conditions from 0 to 100 mM; (a) sulfate (SO₄²⁻), (b) phosphate (HPO₄²⁻), (c) carbonate (CO₃²⁻), (d) the Cl₂ generation rates, and (e) the current efficiencies.

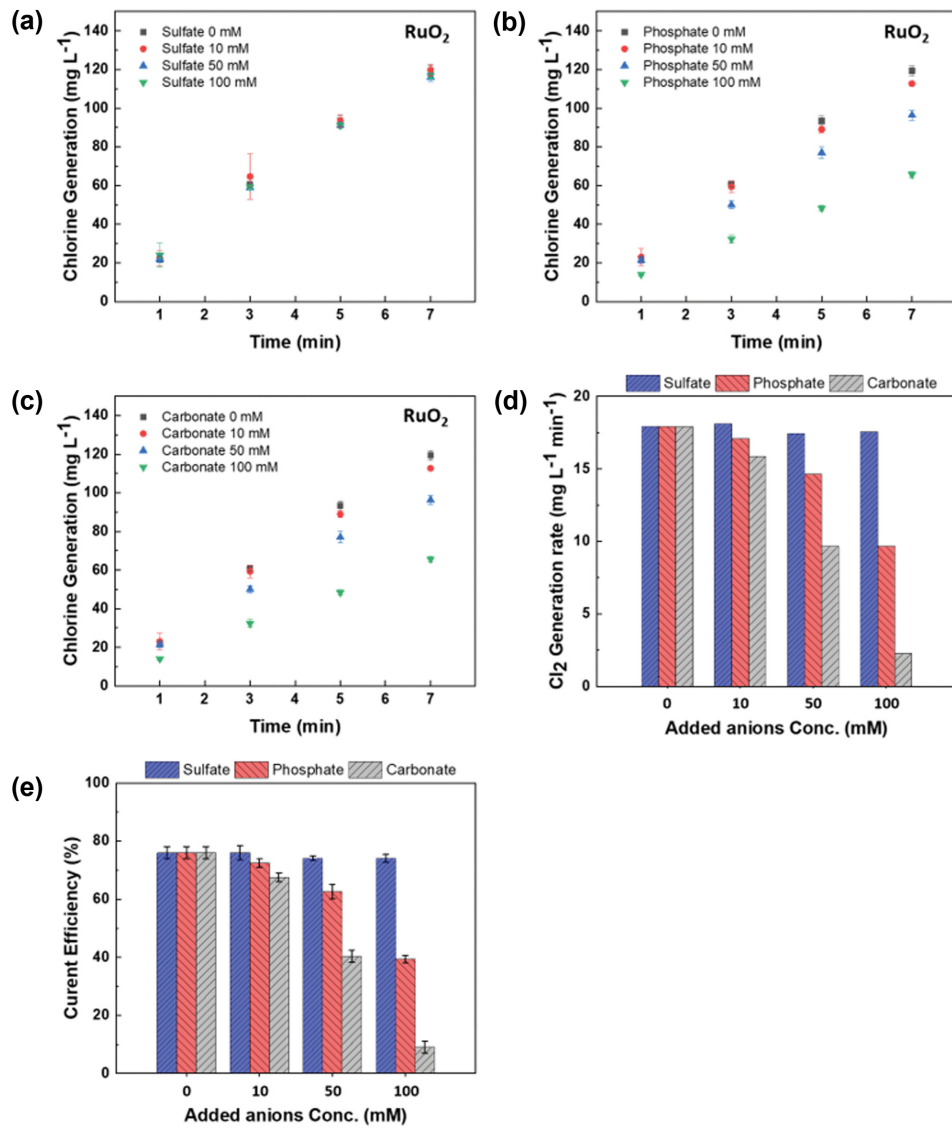


Fig. S2. Chlorine (Cl_2) evolution performance on RuO_2 NTA in various anions conditions from 0 to 100 mM; (a) sulfate (SO_4^{2-}), (b) phosphate (HPO_4^{2-}), (c) carbonate (CO_3^{2-}), (d) the Cl_2 generation rates, and (e) the current efficiencies.