Formation of chlorate and perchlorate during electrochemical oxidation by Magnéli phase Ti$_4$O$_7$ anode: inhibitory effects of coexisting constituents

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Formation of chlorate (ClO$_3^-$) and perchlorate (ClO$_4^-$) as by-products in electrooxidation process has raised concern. In the present study, the formation of ClO$_3^-$ and ClO$_4^-$ in the presence of 1.0 mM Cl$^-$ on boron doped diamond (BDD) and Magnéli phase titanium suboxide (Ti$_4$O$_7$) anodes were evaluated. The Cl$^-$ was transformed to ClO$_3^-$ (temporal maximum 276.2 μM) in the first 0.5 h on BDD anodes with a constant current density of 10 mA cm$^{-2}$, while approximately 1000 μM ClO$_4^-$ was formed after 4.0 h. The formation of ClO$_3^-$ on the Ti$_4$O$_7$ anode was slower, reaching a temporary maximum of approximately 350.6 μM in 4.0 h, and the formation of ClO$_4^-$ was also slower on the Ti$_4$O$_7$ anode, taking 8.0 h to reach 780.0 μM. Compared with the BDD anode, the rate of ClO$_3^-$ and ClO$_4^-$ formation on the Ti$_4$O$_7$ anode were always slower, regardless of the supporting electrolytes used in the experiments, including Na$_2$SO$_4$, NaNO$_3$, Na$_2$B$_4$O$_7$, and Na$_2$HPO$_4$. It is interesting that the formation of ClO$_4^-$ during electrooxidation was largely mitigated or even eliminated, when methanol, KI, and H$_2$O$_2$ were included in the reaction solutions. The mechanism of the inhibition on Cl$^-$ transformation by electrooxidation was explored.

Electrooxidation (EO) process is a promising technology in wastewater treatment$^{1-4}$. EO process has been demonstrated to be a viable means to decompose a broad spectrum of recalcitrant organic pollutants that are not removable by conventional treatment processes, including pharmaceuticals, endocrine disruptors, phenolic compounds, and particularly per- and polyfluoroalkyl substances (PFASs)$^{5-9}$. EO is a chemical destructive technology that promotes organic pollutants degradation by direct electron transfer from organic contaminants to the anode and attack by hydroxyl free radicals and other reactive oxygen species that are also generated on the anode surfaces during the EO process$^{10}$. Sufficiently stable and effective anode materials for EO water treatment have been developed in the last decades, including mixed oxides, such as iridium and/or ruthenium oxides$^{11-13}$, titanium dioxide$^{14}$, and doped diamond electrodes (BDD)$^{15-17}$. This is one of the important reasons why the EO process has approached to technical maturity only recently$^{18}$. Magnéli phase titanium sub-oxides, such as Ti$_4$O$_7$, have recently been explored as promising electrode materials for EO applications because of their high conductivity and chemical inertness. Ti$_4$O$_7$-anodes have been shown to oxidize recalcitrant contaminants by a combination of direct electron transfer (DET) and indirect reactions with HO· produced at the anode surface from water oxidation$^{19}$. Our recent studies have demonstrated the degradation and mineralization of Perfluorooctanesulfonate (PFOS, the one most commonly used per-fluoroalkyl acids) on the Magnéli phase Ti$_4$O$_7$ anode$^{19,20}$. One factor limiting the application of EO in water/wastewater treatment is that its strongly oxidizing conditions also result in the formation of toxic by-products in the presence of Cl$^-$, such as chlorate (ClO$_3^-$) and perchlorate (ClO$_4^-$). In particular, ClO$_4^-$ is difficult to remove from water and its consumption has been linked to health

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risks associated with disruption of the endocrine and reproductive systems. These risks have caused the U.S. Environmental Protection Agency (EPA) to regulate perchlorate under the Safe Drinking Water Act, although an established federal limit has not yet been set. The formation of ClO₃⁻ was reported during EO using several anode materials (e.g., BDD and Ti₃O₇). The presence of Cl⁻ lead to the formation of free chlorine (HOCl) that is further converted to ClO₃⁻ and ClO₄⁻ in EO systems using both BDD and Ti₃O₇ anodes. This transformation process appeared much faster on BDD than Ti₃O₇ anode. It is desirable to develop electrooxidation systems that minimize the formation of chlorine-related toxic by-products for water/wastewater treatment applications.

The purpose of this study was to systematically investigate the formation of ClO₃⁻ and ClO₄⁻ in solutions containing Cl⁻ during electrooxidation on Magneli phase Ti₃O₇ anode and compares it to those on BDD anode. The experiments were performed in different supporting electrolytes at different electrochemical conditions. The effects of a few co-existing constituents were assessed to investigate the inhibition of ClO₃⁻ and ClO₄⁻ formation on the Ti₃O₇ anode. The findings provide a basis for devising strategies to reduce the formation of ClO₃⁻ and ClO₄⁻ in EO on Ti₃O₇ anode.

Materials and methods
Reagents and materials. All chemicals used in the experiments were of reagent grade or higher. ClO₃⁻ was purchased from Sigma-Aldrich (St. Louis, MO). ClO₄⁻, NaCl, and HPLC grade methanol (MeOH) were obtained from Fisher Chemical. Na₂SO₄, NaNO₃, Na₂B₄O₇, Na₂HPO₄, NaH₂PO₄, H₃PO₄, H₂O₂, and KI were supplied by J.T. Baker. All stock solutions were prepared in ultrapure water (18.2 MΩ cm⁻¹) produced by a Barnstead Nano pure water purification system.

Experimental procedures. EO experiment was carried out in an undivided rectangular cell (10 cm × 5 cm × 2.5 cm) made of acrylic materials. A ceramic plate Ti₄O₇ (10 cm × 5 cm) or a Ti/BDD plate of the same size (both sides coated, NeoCoat, Switzerland) was used as the anode, and two 304 stainless steel plates of the same size as the anode, placed on both sides of the anode in parallel with an interval of about 2.5 cm, were used as the cathodes. The Ti₃O₇ electrodes were fabricated according to the method used in our previous study, and information on their preparation and characterization is described in detail in Supporting Information (Text S1). During each experiment, the electrolytic cell contained a 200 mL solution containing Cl⁻ (1.0 mM) and Na₂SO₄ (100 mM) or other salts (NaNO₃, Na₂B₄O₇, Na₂HPO₄, NaH₂PO₄, H₂O₂) as supporting electrolytes stirred at 700 rpm unless otherwise specified. Some EO experiments were performed to explore the impact of pH with Na₂HPO₄, electrolyte as a buffer for pH 10–11, Na₂HPO₄ + Na₃HPO₄ for pH 6–7, and H₂O₂ for pH 2–3. In some EO experiments, MeOH (10–1000 mM), KI (20–100 mM) or H₂O₂ (100–1000 mM) were spiked to the electrolyte solution to explore their impact on the formation of chlorate and perchlorate. All EO experiments were conducted at room temperature.

A constant electric current was supplied at the of 10 mA cm⁻² density using a controllable DC power source (Electro Industries Inc., Monticello, MN), unless otherwise specified. The submerged surface area on both sides of the anode (total geometric surface area was 78 cm²) was used for calculating the electric current density. A CHI 660E electrochemical workstation (CH Instruments, Inc., Austin, TX) was used to measure the anodic potential using an Ag/AgCl reference electrode placed close to the anode, with the potential drop in solution (iRs) compensated. Triplicate samples (1.0 mL each) were withdrawn at pre-selected time points, with the power source paused and the solution continuously stirred to ensure homogeneity. The samples were stored at 4°C until further analysis. The data were plotted with error bars representing the maximum and minimum of duplicated test results. The temperature of solution was monitored and no significant change was found during electrodissolution process.

Analysis methods. Free chlorine, ClO₃⁻, and ClO₄⁻ were quantified in selected samples. The Concentration of HOCl was measured by spectrophotometer at 510 nm (Beckman Coulter DU 800, Brea, CA). A 2.5-mL aliquot sample was immediately mixed with 0.25-M DPD solution (8.0 mM). DPD is oxidized by HOCI to show a red color. ClO₃⁻ and ClO₄⁻ were analyzed using a Waters (Milford, MA) ultra-high performance liquid chromatography with an electrospray ionization (ESI) source (UPLC-MS/MS). Detailed UPLC-MS/MS analytical parameters can be found in Text S2. Quantification of the ClO₃⁻ and ClO₄⁻ was based on multipoint standard calibration.

Results and discussion
Formation of ClO₃⁻ and ClO₄⁻ in EO systems. Cl⁻ can be oxidized in EO systems to form reactive chlorine species that lead to ClO₃⁻ and ClO₄⁻. It was shown that the presence of 1.0-mM Cl⁻ resulted in increased HOCl, ClO₃⁻, and ClO₄⁻ on BDD and Ti₃O₇ anodes (Fig. 1). Almost no appreciable HOCl was detected during the 4.0 h electrooxidation process on the BDD anode, while the concentration of HOCl increased continuously in the system with Ti₃O₇ anode and reached 103.2 μM at 8.0 h. In both systems, ClO₃⁻ concentration increased and then plateaued, while the concentration of ClO₄⁻ increased continuously. The transformation of Cl⁻ was faster on BDD anode in general. The data (Fig. 1) indicate that the concentration of ClO₃⁻ reached 276.2 μM in the first 0.5 h and then decreased on BDD anode, while almost all Cl⁻ (about 1000 μM) was transformed to ClO₄⁻ within 4 h. The formation of ClO₄⁻ on Ti₃O₇ electrode was slower, reaching a plateau of ~ 350.6 μM in 4.0 h and then decreasing slowly. The formation of ClO₄⁻ also appeared to be more slowly on Ti₃O₇ electrode, taking about 8.0 h to reach 780.0 μM.

Cl⁻ can be transformed in electrooxidation by direct electron transfer (DET) to ClO₃⁻ and ClO₄⁻ through a pathway of multiple steps (R1–R3). Direct oxidation of Cl⁻ on BDD electrode generated Cl₂ and hypochlorite. However, unlike BDD electrode, the oxidation of Cl₂ due to DET on Ti₃O₇ anode was not as effective, thus
resulting in slower formation of $\text{ClO}_3^-$ and $\text{ClO}_4^-$ than on BDD anode. Note that indirect routes (R4–R5) can lead to $\text{Cl}^-$ generation on both Ti$_4$O$_7$ and BDD anode, which can further go through the reactions in R2 and R3 to form HOCl and chlorinated by-products. The conversion of $\text{Cl}^-$ to HOCl and the chlorinated byproducts via both DET and indirect routes involves the hydroxyl radicals ($\text{HO}^-$) that are formed by water oxidation on anode.

$$\equiv \text{S} + \text{Cl}^- \rightarrow \equiv \text{S(ads)} + e^- \quad \text{(R1)}$$

$$\text{Cl}^- + \text{HO}^- \rightarrow \text{OCl}^- \quad \text{(R2)}$$

$$\text{ClO}_2^- \rightarrow \text{ClO}_4^- \quad \text{(R3)}$$

$$\text{HO}^- + \text{Cl}^- \leftrightarrow \text{ClHO}^- \quad k = 4.3 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \quad \text{(R4)}$$

$$\text{Cl}^- + \text{HO}^- \rightarrow \text{ClO}_3^- \quad \text{(R5)}$$

The rate of $\text{Cl}^-$ conversion to chlorate and perchlorate in EO systems has been simulated using a model of two sequential steps by assuming each step as pseudo-first-order kinetics (R6–R7). The rate constants $k_1$ and $k_2$ in such sequential equations were obtained by fitting the data as shown in Fig. 1a and b using the software Kintecus v6.80. The values of $k_1$ and $k_2$ were fitted to be $5.40 \times 10^{-4}$ and $7.16 \times 10^{-4}$ s$^{-1}$, respectively, on the BDD anode, while for Ti$_4$O$_7$ anode the values were $8.59 \times 10^{-5}$ and $1.34 \times 10^{-4}$ s$^{-1}$, respectively. This indicates that $\text{Cl}^-$ is oxidized to $\text{ClO}_3^-$ and $\text{ClO}_4^-$ more easily on BDD, evidenced by the larger $k_1$ and $k_2$ on the BDD anode than on Ti$_4$O$_7$ anode. Retarded formation of $\text{ClO}_3^-$ and $\text{ClO}_4^-$ makes it advantageous to apply Ti$_4$O$_7$ anodes in water/wastewater treatment.

$$\text{Cl}^- \rightarrow \text{ClO}_3^- \quad k_1 = - \frac{dc_{\text{Cl}^-}}{dt} \quad \text{(R6)}$$

$$\text{ClO}_3^- \rightarrow \text{ClO}_4^- \quad k_2 = - \frac{dc_{\text{ClO}_3^-}}{dt} \quad \text{(R7)}$$

**Effects of electrolytes on the formation of $\text{ClO}_3^-$ and $\text{ClO}_4^-$.** A set of experiments were performed to evaluate the $\text{ClO}_3^-$ and $\text{ClO}_4^-$ formation by EO with BDD and Ti$_4$O$_7$ anode in solutions containing different supporting electrolytes, including 100-mM Na$_2$SO$_4$, NaNO$_3$, Na$_2$B$_4$O$_7$, and Na$_2$HPO$_4$. The concentrations of $\text{ClO}_3^-$ and $\text{ClO}_4^-$ measured in different electrolyte solutions are summarized in Fig. 2. As shown in Fig. 2a and b, $\text{ClO}_4^-$ concentration reached 990 $\mu$M after 4.0 h with BDD anode and Na$_2$SO$_4$ as supporting electrolyte, which accounts for about 99% of the total $\text{Cl}^-$ initially included in the solution. Almost no $\text{ClO}_3^-$ was detected. At the same current density, the formation of $\text{ClO}_4^-$ was slower with NaNO$_3$, Na$_2$B$_4$O$_7$, and Na$_2$HPO$_4$ as supporting electrolytes on the BDD electrode. It is known that sulfate radical (SO$_4^-$) can be formed by one-electron oxidation of sulfate ion at the anode, which can participate in the oxidation of organics and chloride. Occurrence of peroxodiphosphate was observed during the electrolysis of solutions containing phosphate with BDD.
anodes\textsuperscript{28}. Hence, there could be competitive oxidation reactions from phosphate, although peroxodisulphate was also formed in sulfate containing solution\textsuperscript{29}. The use of NaNO\textsubscript{3} as an electrolyte can promote the formation of ammonium and other reduced nitrogen species by electrochemical reduction\textsuperscript{30}. Ammonium can react with free chlorine, favoring the formation of chloramines and reducing the potential formation of chlorate and perchlorate\textsuperscript{31–33}.

Overall, the transformation was more rapid on BDD anode in all the supporting electrolyte solutions. As shown in Fig. 2, the total ClO\textsubscript{3}\textsuperscript{−} and ClO\textsubscript{4}\textsuperscript{−} concentration was lower when Ti\textsubscript{4}O\textsubscript{7} was used as the anode. For example, the ClO\textsubscript{3}\textsuperscript{−} concentrations were 572.62 and 527.92 μM, respectively, after 4.0 h on the BDD anode with NaNO\textsubscript{3} and Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} as supporting electrolytes, while on Ti\textsubscript{4}O\textsubscript{7} anode, they were 92.37 and 212.84 μM, respectively. In particular, the ClO\textsubscript{4}\textsuperscript{−} concentration in BDD system was 572.6 μM after 4.0 h with NaNO\textsubscript{3} as the supporting electrolyte, while it was only 92.4 μM at the same condition on the Ti\textsubscript{4}O\textsubscript{7} anode.

Inhibitory effect of co-existing constituents. Experiments were performed to examine EO in the presence of Cl\textsuperscript{−} as well as a few co-existing constituents, including MeOH, H\textsubscript{2}O\textsubscript{2} and KI, so as to investigate the effect of the coexisting constituents on the formation of ClO\textsubscript{3}\textsuperscript{−} and ClO\textsubscript{4}\textsuperscript{−} with Ti\textsubscript{4}O\textsubscript{7} anode.

MeOH. Ion exchange resin (IXR) exchange/adsorption has been shown effective to remove PFAS from water. Regeneration of PFAS-laden IXR generates a low-volume, high-concentration liquid waste known as still bottoms that contains high concentrations of PFASs, salts, and residual organic content, including MeOH that is often used as organic co-solvent for IXR regeneration. Our recent studies showed that the MeOH content in still bottoms may play a role in chloride oxidation\textsuperscript{20}. In this section, we designed experiments to further explore the effects of MeOH during the transformation of Cl\textsuperscript{−} by EO. As such, the EO experiment was performed in 100-mM Na\textsubscript{2}HPO\textsubscript{4} solutions containing 1.0 mM Cl\textsuperscript{−} and varying quantities of MeOH. The addition of MeOH appeared to impact the conductivity of the reaction solution slightly. The conductivity dropped from 10.51 mS cm\textsuperscript{−1} to 9.79 mS cm\textsuperscript{−1}, but the anodic potential increased at the same current density (10 mA cm\textsuperscript{−2}) (Fig. S1a), from 2.93 V in the absence of MeOH increasing to 3.22 V with 100 mM MeOH. The presence of MeOH decreased the conductivity of the solution, and thus anodic potential increased at the same current density. The formation of ClO\textsubscript{3}\textsuperscript{−} and ClO\textsubscript{4}\textsuperscript{−} during EO treatment at 10 mA cm\textsuperscript{−2} is displayed in Fig. 3. In the absence of MeOH, ClO\textsubscript{3}\textsuperscript{−} reached 117.8 μM in about 1.0 h and then decreased. The value decreased to 17.3 and 0.0 μM containing 10 mM and 100 mM MeOH, respectively. Such a time course profile indicates the further reaction of ClO\textsubscript{3}\textsuperscript{−}. The formation of ClO\textsubscript{4}\textsuperscript{−} increased monotonically, reaching 329.0 μM in 8.0 h in the absence of MeOH. When 10 mM and 100 mM MeOH were spiked, almost no ClO\textsubscript{4}\textsuperscript{−} were formed for the first 2.0 h, after which ClO\textsubscript{4}\textsuperscript{−} started to increase, reaching 300.0 μM and 251.8 μM in 8.0 h, respectively. The formation of ClO\textsubscript{4}\textsuperscript{−} was completely inhibited when 1000 mM MeOH was added, indicating that MeOH inhibited the formation of ClO\textsubscript{3}\textsuperscript{−} and ClO\textsubscript{4}\textsuperscript{−}. Delayed formation of ClO\textsubscript{4}\textsuperscript{−} in the presence of lower MeOH dosage (10 and 100 mM) may be caused by MeOH depletion over time. Formation of ClO\textsubscript{3}\textsuperscript{−} and ClO\textsubscript{4}\textsuperscript{−} was neither observed in acid or neutral conditions when 1000-mM MeOH was spiked, by respectively using 50-mM NaH\textsubscript{2}PO\textsubscript{4} + 50-mM Na\textsubscript{2}HPO\textsubscript{4} (pH 6–7) or 100-mM H\textsubscript{3}PO\textsubscript{4} (pH 2–3) as electrolytes instead of Na\textsubscript{2}HPO\textsubscript{4} (pH 10–11).

A prior study proved that Cl\textsuperscript{−} was not oxidized to Cl\textsuperscript{2−} via DET on the Ti\textsubscript{4}O\textsubscript{7} anode, while Cl\textsuperscript{2−} was formed mainly through the indirect pathways (R4–RS)\textsuperscript{24}. Cl\textsuperscript{2−} reacts with another Cl\textsuperscript{−} to form Cl\textsubscript{3}−. Cl\textsuperscript{−} and Cl\textsubscript{3}− also combine with each other to form free chlorine (Cl\textsubscript{2}, HOCl)\textsuperscript{32,34,35}. These reactive chlorine species may accumulate and diffuse away from the anode surface, and finally convert into ClO\textsubscript{3}− and ClO\textsubscript{4}−. MeOH can transform HO· into perhydroxyl radicals (with a second-order rate constant is 2.1 × 10\textsuperscript{9} M\textsuperscript{−1} s\textsuperscript{−1}). Meanwhile, the reaction rate
constant between MeOH and Cl· is $5.7 \times 10^9$ M$^{-1}$ s$^{-1}$. MeOH could consume Cl· in the bulk solution and HO· (if present). The formation of ClO$_3^-$ and ClO$_4^-$ was thus reduced with low concentrations of MeOH, while a high concentration of MeOH can rapidly transform Cl·, inhibiting the generation of ClO$_3^-$ and ClO$_4^-$. 

H$_2$O$_2$. Yang et al. found that the formation of ClO$_4^-$ during EO with BDD anode can be largely inhibited by adding H$_2$O$_2$. Therefore, H$_2$O$_2$, a commonly used quenchers were also investigated in this study. The time-course data of ClO$_3^-$ and ClO$_4^-$ formation in the presence of H$_2$O$_2$ are shown in Fig. S2. Using Kintecus v6.80, the data in Fig. S2 were fit to obtain $k_1$ and $k_2$ represented in equation R6–R7, and they were $9.78 \times 10^{-5}$ and $7.09 \times 10^{-4}$ s$^{-1}$, respectively, in the absence of co-existing constituents (Fig. 4). The values of $k_1$ and $k_2$ decreased to $1.16 \times 10^{-6}$ and $1.87 \times 10^{-4}$ s$^{-1}$ when 1000-mM H$_2$O$_2$ were spiked, respectively. The data shown in Fig. S2 and Fig. 4 also showed that addition of H$_2$O$_2$ at 1000 mM also significantly limited ClO$_3^-$ and ClO$_4^-$ formation during the EO.

H$_2$O$_2$ is known to be both an oxidant (H$_2$O$_2$/H$_2$O, $E^0 = 1.76$ V) and a reductant (O$_2$/H$_2$O$_2$, $E^0 = 0.68$ V) depending on the composition of the reaction media. Thus, Earlier studies have demonstrated that HOCl can be reduced back to Cl$^-$ by H$_2$O$_2$. In addition to free chlorine, H$_2$O$_2$ can also react with the chlorine radical species directly (R10-R11). Thus, it is presumed that the reduction of HOCl and chlorine radical species by H$_2$O$_2$ outweighed the oxidation of Cl$^-$ by H$_2$O$_2$ in the EO system, and thus decreased ClO$_3^-$ and ClO$_4^-$ formation. Moreover, H$_2$O$_2$ may react with ClO$_3^-$ to form chlorine dioxide (R12), thus further reducing the formation of ClO$_3^-$. 

\begin{equation}
\text{HOCl} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Cl}^- + \text{H}_2\text{O} + \text{O}_2 \quad k = 1.1 \times 10^4 \text{ M}^{-1}\text{s}^{-1} \tag{R8}
\end{equation}
KI, Cl⁻ (Cl₂Cl⁻, 2.41 V) and Br⁻(Br₂Br⁻, 1.62 V) can be oxidized by HO· to form carcinogenic chlorate and bromate ⁴⁰, while I⁻, having a lower reduction potential of 1.33 V ²⁵,⁴¹, may be more readily oxidized than Cl⁻ and Br⁻ in theory ⁴². It was also found in our previous studies that NaI may be used as a Cl⁻ free salt to regenerate PFAS-laden ion exchange resin without compromised capability in PFAS recovery ²⁰. To evaluate the impact of I⁻ on the formation of ClO₃⁻ and ClO₄⁻ during EO process, an EO experiment was performed in the presence of I⁻. It should be noted that the anodic potential was relatively constant at the same current density (10 mA cm⁻²) with I⁻ at different levels (Fig. S1b). The presence of I⁻ inhibited the formation of ClO₃⁻ and ClO₄⁻ significantly as shown in Fig. 5. Almost no ClO₃⁻ was formed during the first 4.0 h and then increased to 25.5 μM after 8.0 h in the presence of 20-mM KI. Similarly, the formation of ClO₄⁻ increased slowly during the first 4.0 h and reached 287.2 μM at 8.0 h. Furthermore, near-complete inhibition of ClO₃⁻ and ClO₄⁻ formation was achieved when 100 mM KI was spiked, with the values of k₁ and k₂ decreased to 0 and 4.76 × 10⁻⁶ s⁻¹, respectively (Fig. 4). This suggests that I⁻ outcompetes Cl⁻ for reaction with HO·, leading to a slower generation of HOCl on Ti₄O₇, and thus inhibiting the formation of ClO₃⁻ and ClO₄⁻. I⁻ can be oxidized by common oxidants leading to reactive iodine species (e.g., hypoiodous acid (HOI), iodine (I₂), and iodide radical (I·)), and then to iodate (IO₃⁻), which is not considered carcinogenic because it is rapidly reduced to I⁻ after being ingested ⁴³,⁴⁴.

Conclusions
In conclusion, oxidation of Cl⁻ lead to the formation of ClO₃⁻ and ClO₄⁻ on both BDD and Magnéli phase Ti₄O₇ anode during EO. This transformation process was much faster on BDD than Ti₄O₇ anode in different supporting electrolytes, including Na₂SO₄, NaNO₃, Na₂B₄O₇, and Na₂HPO₄. The formation of ClO₃⁻ and ClO₄⁻ was easier with Na₂SO₄ as supporting electrolyte in both systems. Around 99% and 58% of the total Cl⁻ was transformed to ClO₃⁻ after 4.0 h of EO with the BDD and Ti₄O₇ anode, respectively. When NaNO₃ was used as electrolytes, ClO₃⁻ and ClO₄⁻ formation was decreased to some extent, with only 9% of the total Cl⁻ transformed to ClO₃⁻ on Ti₄O₇ anode. Addition of MeOH, H₂O₂, and KI can effectively inhibit the formation of ClO₃⁻ and ClO₄⁻ during EO by Ti₄O₇ anode. Near complete inhibition of their formation was achieved with 1000-mM MeOH and 100-mM KI present. MeOH, H₂O₂, and KI appear to be ideal quenchers to mitigate ClO₃⁻ and ClO₄⁻ formation, because they are effective, accessible and inexpensive. In particular, KI is more stable and easier to be stored and transported than MeOH and H₂O₂. I⁻ is oxidized to iodate ultimately in the EO system, while iodate is a relatively stable and benign chemical. In practice, the EO treatment can be designed to fully convert I⁻, or else a polishing step, such as IXR, has to be followed to remove remaining I⁻. The findings provide a basis for devising strategies to reduce the formation of ClO₃⁻ and ClO₄⁻ in the EO process.

Figure 5. Formation of ClO₃⁻ and ClO₄⁻ during the electrochemical oxidation of Cl⁻ in the presence of KI on Ti₄O₇ anodes. Conditions: [Cl⁻]₀ = 1.0 mM, [Na₂HPO₄] = 100 mM, current density = 10 mA cm⁻².

\[
\text{Cl}_2 + 2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{HCl} \quad k = 1.3 \times 10^4 \text{M}^{-1}\text{s}^{-1} \quad (R9)
\]
\[
\text{Cl}^- + \text{H}_2\text{O}_2 \rightarrow \text{HOCl} + \text{Cl}^- + \text{H}^+ \quad k = 2.0 \times 10^9 \text{M}^{-1}\text{s}^{-1} \quad (R10)
\]
\[
\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{HOCl} + 2\text{Cl}^- + \text{H}^+ \quad k = 1.4 \times 10^5 \text{M}^{-1}\text{s}^{-1} \quad (R11)
\]
\[
2\text{H}^+ + 2\text{ClO}_3^- + \text{H}_2\text{O}_2 \rightarrow 2\text{ClO}_2 + 2\text{H}_2\text{O} + \text{O}_2 \quad (R12)
\]
Data availability

The SEM collected during the current study is available in the NoMad repository, 8uLLHSolQ06aHg2roegwpg.

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**Author contributions**
L.W. wrote the mani manuscript. Q.H. revised and edited. All authors reviewed the manuscript.

**Competing interests**
The authors declare no competing interests.

**Additional information**
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