Fabrication and Characterization of the Porous Ti₄O₇ Reactive Electrochemical Membrane

Guangfeng Qi¹,²†, Xiaohui Wang¹,²*, Jingang Zhao¹,², Chunyan Song¹,², Yanbo Zhang¹,², Feizhou Ren¹,² and Nan Zhang¹,²

¹Technical Test Center of Sinopec Shengli OilField, Dongying, China, ²Testing and Evaluation Research Co. Ltd. of Sinopec Shengli OilField, Dongying, China

Preparation of the Magnéli Ti₄O₇ reactive electrochemical membrane (REM) with high purity is of great significance for its application in electrochemical advanced oxidation processes (EAOPs) for wastewater treatment. In this study, the Ti₄O₇ REM with high purity was synthesized by mechanical pressing of TiO₂ powders followed by thermal reduction to Ti₄O₇ using the Ti powder as the reducing reagent, where the TiO₂ monolith and Ti powder were separated from each other with the distance of about 5 cm in the vacuum furnace. When the temperature was elevated to 1333 K, the Magnéli phase Ti₄O₇ REM with the Ti₄O₇ content of 98.5% was obtained after thermal reduction for 4 h. Noticeably, the surface and interior of the obtained REM bulk sample has a homogeneous Ti₄O₇ content. Doping carbon black (0wt%-15wt%) could increase the porosity of the Ti₄O₇ REM (38–59%). Accordingly, the internal resistance of the electrode and electrolyte and the charge-transfer impedance increased slightly with the increasing carbon black content. The optimum electroactive surface area (1.1 m²) was obtained at a carbon black content of 5wt%, which increased by 1.3-fold in comparison with that without carbon black. The as-prepared Ti₄O₇ REMs show high oxygen evolution potential, approximately 2.7 V/SHE, indicating their appreciable electrocatalytic activity toward the production of •OH.

Keywords: Ti₄O₇, reactive electrochemical membrane, Ti, TiO₂, thermal reduction

1 INTRODUCTION

Ceramic porous sub-stoichiometric Ti oxides (TiₙO₂₋₄, 4≤n≤10), known as Magnéli phases, were first synthesized and characterized in the 1950s (Zhou et al., 2018). Among these oxides, Ti₄O₇ exhibits excellent performance owing to its unique structure, e.g., excellent corrosion resistance and outstanding electrical conductivity with a value of 1000 S cm⁻¹, which is higher than the 727 S cm⁻¹ of graphitized carbon (Walsh and Wills, 2010). In light of this, the Ti₄O₇ material has been widely used as a cathodic protection during the electrodeposition process, in batteries as either an electrode material or an additive to the active materials (Zhang et al., 2017). In addition, due to its stability under anodic polarization and high oxygen evolution overpotential, Ti₄O₇ has been recently utilized as the inert anode material for weekly sorbed •OH production in the field of electrochemical wastewater treatment, which shows comparable electrocatalytic activity to the boron-doped diamond (BDD) anode for pollutant degradation (Bejan et al., 2009).

Recently, depositing Ti₄O₇ films at the Ti surface has been manufactured successfully by the plasma coating approach, which is a widely spread technology for many types of applications (corrosion protection, abrasion resistance, thermal barriers, etc.) (Ganiyu et al., 2016; Oturan et al.,...
2017). This preparation process is mainly proceeded by two steps: 1) reduction of TiO2 with coke to produce Ti4O7 powder and 2) plasma elaboration of Ti4O7 on the Ti-alloy substrate at 10,000–15,000°C accompanied by conversion of all sub-oxides of Ti to Ti4O7 [46]. However, the application of this Ti4O7 electrode is greatly limited by mass diffusion since there is a thick stagnant boundary layer (~100 μm) at the plate electrode surface (Liu and Vecitis, 2012; Zaky and Chaplin, 2013). The flow-through mode, which is defined as operating with convective flow perpendicular to the porous electrode surface, allowed for enhanced mass transport rates relative to the traditional parallel flow mode by restricting the diffusional distance of reactants to a length-scale on the order of the pore radius of the electrode (Vecitis et al., 2011; Zaky and Chaplin, 2013; Guo et al., 2016a; Guo et al., 2016b). Thus, significant attention has been recently paid to the integration of membrane filtration and electrochemical process, known as the Ti4O7 reactive electrochemical membrane (REM), for aqueous contaminant degradation because this operation mode promotes the reaction between the contaminant and •OH produced at the anode surface. As a result, REMs based on electrochemical advanced oxidation processes (EAOPs) are a cutting edge class of electrodes that hold great promise in revolutionizing water/wastewater treatment (Zaky and Chaplin, 2013).

As for the preparation of the Ti4O7 REM, TiO2 is typically used as the main feedstock due to its abundance and relatively low cost. The mechanical pressing of Ti4O7 powders, followed by thermal sintering, has been widely used to fabricate the Ti4O7 REMs. There are many conventional approaches available to synthesize the Ti4O7 materials under controlled reducing conditions at relatively high temperature using different reducers such as metals (Kitada et al., 2012), carbon (Ganiyu et al., 2016), carbonaceous organic materials (Guo et al., 2019), and reducing atmosphere (H2 and NH3) (Li et al., 2010; Zhang et al., 2013; Lin et al., 2018). However, most of the production methods are energy and time-consuming. For example, the Ti4O7 REM was synthesized by reduction of commercial TiO2 ultrafiltration membranes at 1333 K for 50 h in the H2 atmosphere (Guo et al., 2016b). As another example, an ultrafiltration membrane layer composed of Ti4O7 and Ti6O11 was obtained by dip-coating of a TiO2 layer on the inner surface of a tubular Al2O3 membrane, followed by a reduction step under 30% H2 in the Ar atmosphere at 1308K for 7 h (Geng and Chen, 2016). High processing temperatures over 1000°C and such long time not only inevitably leads to morphology deformation but also results in particle aggregation and dense low surface area materials, which limit its practical applications as electrode materials, where high surface area, a large number of active sites, and a porous structure are all important for the performance (Lin et al., 2018). In addition to the cases under the reducing atmosphere (H2 and NH3), the as-prepared Ti4O7 REMs did not have high purity since the residual reducing reagents and their derivatives eventually reduce the purity of the obtained Magnéli Ti4O7 REM. However, the gaseous reduction process usually brings about high costs and potential danger. The high preparation costs and rigorously controlled fabrication conditions (H2 atmosphere) might limit their commercial development to some extent. Overall, the control of the stoichiometry of Magnéli phases according to the choice of precursors and thermal treatment is an interesting challenge for material science.

In the present study, thermal reduction of TiO2 by metal Ti under the vacuum condition was developed to prepare the Ti4O7 REM with high purity. The influences of the preparation temperature and thermal sintering time were optimized for Ti4O7 REM preparation. The Ti4O7 REM was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and mercury intrusion porosimetry. The water filtration performance of these REMs was evaluated based on the pressure-normalized permeate flux. In addition, the electrochemical properties of the REMs were studied by sweep voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

2 MATERIALS AND METHODS

2.1 Reagents

TiO2 (99.99%, 25 nm particles) and Ti (99.9%, 10 nm particles) powder were purchased from Beijing Xingyuan Technology Co., Ltd. Carbon black (XC-72R) was bought from Cabot Corporation. Ethanol (EtOH) (99.99%, anhydrous), sodium sulfate (99.9%), potassium ferrocyanide (99.5%), and potassium ferricyanide (99.5%) were obtained from Sigma-Aldrich. All solutions were prepared using deionized water (18.2 MΩ cm−1 at 25°C).

2.2 Ti4O7 REM Fabrication

The Ti4O7 ceramic microfiltration membrane was prepared by the following route: TiO2 powder and carbon black were first mixed together and then put into a ZrO2 ball-milling bowl (500 ml in volume, Fritsch, Germany), where the load of carbon black was set to 7.5% of the mass of the TiO2 powder. A planetary ball-mill (Fritsch, Pulverisette 6, Germany) was utilized to mix the membrane contents, in which the grinding balls were a mixture of Nikkato ZrO2 balls in the diameters of 1, 2, 5, 10, and 20 mm. The volume of the balls and the material account for 1/3 of the volume of the ball mill tank, respectively. Anhydrous ethanol is used as a ball milling agent. After allowing it to dry at 60°C overnight, 10 g powders were mixed with 2–3 wt% of ethanol and transferred to a disc mould and pressed under the pressure of 30 MPa by a hydraulic press (Specac, UK) to form the precursor of the REM. The membrane was first sintered in air for 4 h at 973 K for the removal of carbon black then was reduced in the presence of the Ti powder (about 4 g) in a vacuum (<8 × 10−3 MPa) tube furnace for the preparation of the Ti4O7 REM. The precursor of the Ti4O7 monolith and Ti powder were separated from each other, and the distance is about 5 cm. The heating/cooling rates were both 4 K min−1.

2.3 Physicochemical and Electrochemical Characterization

XRD analysis was performed to obtain the phase information of the Ti4O7 REM. The Scherrer equation was used to calculate the
crystallite size. The Ti$_4$O$_7$ REM surface morphology was characterized by SEM. Mercury intrusion porosimetry was used to investigate the porous structures of the electrodes. The EIS and CV analyses were conducted with an electrochemical workstation (PGSTAT302N, Metrohm) and used a three-electrode setup with the Ti$_4$O$_7$ electrode as the working electrode, a platinum plate electrode (3 cm $\times$ 3 cm) as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. EIS analysis was performed at the open circuit potential (OCP, 190 mV/SCE) over a frequency range of 10$^{-2}$–10$^4$ Hz in 100 mM Na$_2$SO$_4$ supporting electrolyte solution with the presence of 5 mM K$_4$Fe(CN)$_6$ and 5 mM K$_3$Fe(CN)$_6$ redox couple. CV measurements were recorded at a voltage step of 0.05 V in 100 mM NaClO$_4$ electrolyte. The electrochemically active surface area was calculated based on CV analysis at a scan rate from 5 to 30 mV s$^{-1}$ in a potential range of $-0.2$–$0.5$ V.

3 RESULTS AND DISCUSSION

3.1 Ti$_4$O$_7$ REM Fabrication

The effect of thermal reduction temperature on the purity of the Ti$_4$O$_7$ REM was conducted in the range of 1133–1433 K. Figure 1 shows the XRD patterns of the REM samples prepared at various temperatures. It was observed that the color of the REM sample turned from white to light blue after thermal reduction at the reduction temperature of 1133 K. But the obtained REM sample was mainly rutile. This indicates that this reaction temperature was too high to transform anatase-TiO$_2$ to the Magnéli phase. The phase transformation was observed at a sintering temperature of 1233 K, where the predominant phase was Ti$_6$O$_{11}$ and Ti$_5$O$_9$ was the marginal phase. When the temperature was elevated to 1333 K, the XRD patterns show the characteristic peaks for Ti$_4$O$_7$, and almost no peaks for other Magnéli phases suggests that a high purity Magnéli phase Ti$_4$O$_7$ REM was successfully fabricated. At this temperature, the Ti$_4$O$_7$ content of the samples was 98.5%, while the Ti$_3$O$_5$ content was only 1.5%. In contrast, when the reduction temperature was further increased to 1433 K, a single phase of Ti$_3$O$_5$ is formed, indicating that this reaction temperature was too high to synthesize pure Ti$_4$O$_7$.

To further find the optimum conditions for the synthesis of Ti$_4$O$_7$, the influence of thermal reduction time on the purity of the Ti$_4$O$_7$ REM was also studied. The XRD patterns of the as-prepared REM samples prepared at 1333 K for 2, 4, and 6 h were shown in Figure 2. It is found that the Magnéli phase Ti$_4$O$_7$ was the major component at the thermal reduction time of 2–6 h. For 2 h, the as-prepared REM sample contains 24% Ti$_6$O$_{11}$, 10% Ti$_5$O$_9$, and 66% Ti$_3$O$_5$. When the thermal reduction time reached 4 h, XRD patterns show that Ti$_6$O$_{11}$ and Ti$_5$O$_9$ phases disappeared and Ti$_3$O$_5$ to be the main crystalline phase in the material with only <3% Ti$_6$O$_{11}$ left. Extending the reaction time to 6 h, the percentage of Ti$_3$O$_5$ phases increased slightly to 6%, and the percentage of Ti$_4$O$_7$ exhibited an insignificant change. These results mean that the thermal reduction time of 2 h is insufficient for the complete transformation of TiO$_2$ to Ti$_4$O$_7$. However, as for 6 h, the increase of the miscellaneous peak, especially Ti$_3$O$_5$, indicates that the sample proceeded overreduction due to the longer thermal reduction time. These results illustrate the optimum reduction time for preparing the pure Ti$_4$O$_7$ REM was 4 h.

The XRD peaks for the reduced phases are relatively sharp (fwhm = 0.117° for 2 h, 0.084° for 4 h and 0.092° for 6 h) for the peaks at 26.4°, respectively. After accounting for instrumental broadening, the estimated crystallite sizes are 67 nm for 2 h, 90 nm for 4 h, and 119 nm for 6 h according to the Sherrer’s equation, while the crystallite size of the original TiO$_2$ is 25 nm, indicating the crystallite growth. For further investigation of the phase composition of the productions, the XRD spectrums of the REM those were not grounded into powder were showed in Figure 3. In addition, the XRD peaks of the REM were perfectly coincident with those grounded into powder, meaning that the component of the REM bulk was homogeneous. It is noteworthy that as for the common carbothermal reduction approach with mixing carbon powder and TiO$_2$, the surface and interior of the obtained bulk sample show different compositions (Tsumura et al., 2004; Toyoda et al., 2009).

3.2 Pore Properties Modification

The morphology and pore structure of the REM were characterized by SEM Hg porosimetry, respectively. The SEM images in Figures 4A–D show the samples prepared at 1333 K with different carbon black contents of 0wt%, 1.5wt%, 5wt%, and 10wt%. The pore size of four samples was almost similar due to the fact that the grain-growth behavior mainly depends on the sintering time and temperature (Guan et al., 2016). The SEM images of the REM exhibit a three-dimensionally assembled structure with macro porosity, and the crystallites were indeed intimately fused or even consolidated to form large single-crystal particles on the micrometer scale. During the high-temperature reduction process, the agglomerates of solid particles and particle
bonding resulted in the formation of the porous structure inside the cavity in the presence of the porosity-producing agent. Figure 4 shows that the pore size increased with the increasing carbon black content. The size of pores in Figure 4D seems to be larger than that in Figure 4A, which may be explained by the different carbon contents of these two samples. The detailed pore structure of these membranes was characterized by Hg porosimetry, and the results are presented in the Figure 5. It is demonstrated that the REM sample possessed uniform macropores of 0.4–0.5 μm (Figure 6). The almost same macropore diameter and volume indicate that the well-defined macroporous structure of the monolith was retained. These results are consistent with the results of SEM images. Moreover, the REM exhibits a pore size distribution with ~99% of the measured surface area associated with pores <0.5 μm, and essentially, the entire pore volume attributed to pores with 0.2–0.5 μm diameters. As shown in Figure 5, based on the porosimetry results, the porous surface area for the membrane without carbon black was estimated as 1.477 m² g⁻¹ with the porosity(θ) and median pore diameter of 0.382 and 0.380 μm, respectively. As the content of carbon black was elevated to 1.5wt%, the porous surface area was enhanced to 1.797 m² g⁻¹ with the increase in the porosity by 4.7%, while no difference was observed in the pore size as compared with that without the addition of carbon black. The membrane with 5wt% carbon black has a porous surface area of 2.011 m² g⁻¹, median pore diameter of 0.481 μm, and its porosity is 0.427 which is the same with the former. The porosity for the REM with 15wt% carbon black was determined as 0.594, specific surface area of 2.477 m² g⁻¹, and median pore diameter of 0.575 μm. As the volume of carbon black increased, the change of pore size is slight, and the porosity has a gap of 21% between the samples without carbon black and with 15% carbon black. Micron-sized pores dominated the REM pore volume, which facilitates water transport through the REM at low applied pressures and is expected beneficial for facilitating interfacial mass transfer during the electrochemical reaction. Porosimetry analysis results show that the average pore diameter was closed to the median pore diameter (based on pore volume data) showing symmetrically distribution pore size. The addition of high carbon black content was not recommended since it would cause the crack of the REM monolith during the flow-through operation mode.

A flow-through reactor was used to assess the permeation ability of REMs with ultra-pure water experiments which were carried out with the Ti₄O₇ REM. A digital gear pump was prepared to control the permeate flux and a pressure gage was used to record the hydraulic pressure. The evolution of the permeate flux with the carbon black content is plotted in Figure 7. It is found that the porosity and pore size both exerted the influence on the permeate flux. The REM without carbon black and with 1.5%wt carbon black have the same pore...

**Figure 2** | (A) XRD patterns of the as-prepared samples obtained at 1333 K for 2, 4, and 6 h; (B) Phase composition percentage.

**Figure 3** | XRD patterns of the surface and interior of the REM monolith.
size of 380 nm but different porosity, e.g., 38 and 42%, respectively. The permeate flux of the latter increased 28% than the former. REMs with 1.5wt% and 5wt% carbon black have the same porosity of 0.42 and different pore size. With the bigger pore size and porosity, the increased extent of the permeate flux was much more evident. The permeate flux for the sample with the pore size of 480 nm increased by 57% than the sample with 380 nm pore size. The results of the REM membrane with 60% porosity and 580 nm pore size showed that the method improved the flux obviously with a 452% increase in the flux from 250 to 1379 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ than the original REM membrane. This indicates that a high content of carbon black was a crucial factor for the permeation ability of the REM membrane.

The resistance-in-series model was applied to evaluate the characteristics of the membrane flux; according to the Darcy law, the permeation flux ($J$) takes the following form:

$$J = \frac{\Delta P}{\eta R_m}, \quad (1)$$

where $J$ is the permeation flux (L/m$^2$ h), $\Delta P$ (Pa) is the transmembrane pressure, $\eta$ is the dynamic viscosity of the permeate, and $R_m$ (m$^{-1}$) is the intrinsic membrane resistance. Table 1 made a summary of pressure-normalized permeate fluxes (LMH/bar) and intrinsic membrane resistance ($10^{10}$/m) of the four samples. It can be seen that $R_m$ decreased with the increases of the carbon black content. $R_m$ of the original membrane is ~6 times higher than that of the membrane with 15 wt% content of carbon black, which suggest that a lower membrane resistance can be achieved by simply increasing the content of carbon black.

### 3.3 Electrochemical Characterization

The measurements of the electrochemically active surface area of each electrode were conducted within the potential region between hydrogen and oxygen evolution reaction, i.e., $-0.2$ to $-0.5$ V/SCE, at the sweep rates of $5$ to $30$ mV/s. As shown in Figure 8, the capacitive current decreases linearly with lowering sweep rates so that the apparent capacitance can be calculated from the slope of the charging current $vs$ sweep rate. The double layer capacitances ($C_{dl}$) were determined based on the CV test according to Eq. 2.

$$\frac{I_a - I_c}{2} = C_{dl} \nu, \quad (2)$$

where $I_a$ and $I_c$ represent the measured plateau currents at 0.25 V/SCE, and $\nu$ is the scan rate (V/s). The surface roughness factor and electroactive surface area were calculated according to the previous study with the use of the electrode geometric surface area. Assuming a double layer capacitance of 60 μF/cm$^2$ for a surface of oxides, the roughness factors “$r$” can be estimated as follows:

$$r = \frac{C_{dl}}{C_0}, \quad (3)$$
FIGURE 5 | Cumulative pore area and log differential intrusion pore volume of Hg intrusion porosimetry analysis for (A,E) 0wt%, (B,F) 1.5wt%, (C,G) 5wt%, and (D,H) 15wt%.
Comparative cyclic voltammograms of the four REM membranes with a nominal geometric surface area of 3.38 cm² in the potential range of −0.2–0.5 V/SCE are shown in Figure 8. It was calculated that the REM samples without doping carbon black and with 1.5% carbon black have the almost same average roughness (2557–2563). As for 5wt% carbon black, the calculated surface roughness was 3250 and the total electroactive surface area was 1.1 m², which accounted for approximately 54.6% of the porous surface area measured by Hg porosimetry and increased by 1.3-fold in comparison with that without carbon black. However, the REM membrane obtained with doping 15wt% carbon black has the lowest surface roughness at 1953. In summary, the electrochemically active area (i.e., the roughness factor) of the porous Ti₄O₇ electrode is 3 orders of magnitude higher than the apparent surface area of the REM membrane, which was favorable for the electrochemical reaction.

A stepwise increase in potential was implemented by recording the current response to obtain the water oxidation potential in the Na₂SO₄ electrolyte (Figure 9). For Ti₄O₇, there was a negligible response of the current when the potential was below 2.7 V/SHE. Further increasing potential resulted in an apparent enhancement of the current, indicating the potential for water oxidation was within the range of 2.5–2.7 V/SHE. This result was higher than that of the oxygen evolution potential of 2.5 V/SHE reported by Smith et al. and reached the highest reported value of 2.7 V/SHE (Miller-Folk et al., 1989; Graves et al., 1991; Kolbrecka and Przyluski, 1994; Grimm et al., 1998). Thus, we can infer that the as-prepared Ti₄O₇ REM exhibits an appreciable electrocatalytic activity toward the production of •OH.

Figure 9B shows the EIS curves of REMs at room temperature. Each of the curves consists of a straight line (at low frequency) and a depressed semicircle (at high frequency), which are related to the ion diffusion in the bulk of the electrode and the charge transfer process at the electrolyte–electrode interface, respectively. The Rs displays the internal resistance of the electrode and electrolyte, and the charge-transfer impedance (R_{ct}) is expressed vividly by the depressed semicircle in the intermediate frequency region. As shown in Figure 9B and Table 1, Rs values of Ti₄O₇ were estimated to be 17.1 ± 0.17, 17.53 ± 0.18, 18.8 ± 0.19, and 19.6 ± 0.20 Ω, respectively, indicating a minimal difference between the conductivity of these REMs. But it can be seen that as the content of carbon black increased, the value of R_{s} increased, which may be associated with the porosity of the REM membrane samples. The existence of a large number of voids reduced the effective cross-section of current conduction and therefore decreased the conductivity. Notably, the charge transfer resistances (R_{ct}) of these REMs were 3.57 ± 0.36, 3.68 ± 0.37, 4.14 ± 0.41, and 5.19 ± 0.52 Ω, respectively, which were three orders of magnitude smaller than that for the graphite plate electrode (You et al., 2016; Xie et al., 2020), suggesting a much higher charge transfer capacity of Ti₄O₇.

### Table 1: The effect of carbon black content on the property of REM samples.

| Carbon black contents (wt%) | 0     | 1.5   | 5     | 10    |
|----------------------------|-------|-------|-------|-------|
| Pressure-normalized permeate flux (LMH/bar) | 250 ± 10 | 320 ± 1 | 503 ± 12 | 1379 ± 8 |
| Intrinsic membrane resistance (10¹⁰/m)        | 9.25  | 7.3   | 4.83  | 1.59  |
| Determinate coefficient R²                    | 0.9869| 0.9946| 0.9979| 0.9997|

---

**Figure 6**: Porosity and pore size with different carbon black contents.

**Figure 7**: Pressure-normalized permeate fluxes of REMs with different carbon black contents.

**Figure 9B**: Shows the EIS curves of REMs at room temperature.
FIGURE 8 | Determination of double-layer capacitance at different scan rates (5–30 mV s$^{-1}$) for REMs using CV in the 100 mM Na$_2$SO$_4$ electrolyte solution. CV scans: (A) 0wt%, (B) 1.5wt%, (C) 5wt%, and (D) 15wt%. Corresponding plots of charging currents versus scan rates: (E) 0wt%, (F) 1.5wt%, (G) 5wt%, and (H) 15wt%. 

Slope of the plot in (E) is 0.454, with an $R^2$ of 0.999; in (F) it is 0.455, with an $R^2$ of 0.995; in (G) it is 0.577, with an $R^2$ of 0.999; in (H) it is 0.396, with an $R^2$ of 0.998.
3.4 Thermal Reduction Mechanism

In this study, the Ti$_4$O$_7$ REM fabrication process combined the following two steps: 1) the oxygen atoms in the TiO$_2$ monolith reunited to oxygen and then effused into the vacuum environment at the higher reaction temperature and 2) the emanated oxygen is captured by the Ti powder. Thermodynamically, the reaction driving force enables titanium oxidation and TiO$_2$ reduction. For step one, the general reaction can be given as

$$2(n-1)\text{Ti}_n\text{O}_{2n-1}(s) \rightarrow 2n\text{Ti}_{n-1}\text{O}_{2n-3}(s) + O_2(g),$$  \hspace{1cm} (4)

where Ti$_{n-1}$O$_{2n-3}$ and Ti$_n$O$_{2n-1}$ are the closest compounds in the Ti–O binary phase diagram. In these reactions, only oxygen is the gas phase, and others are pure solid. Then, the Gibbs free energy could be written as

$$\Delta_r G = \Delta_r G^\theta + \frac{1}{2} RT \ln \frac{P_{O_2}}{p^\theta},$$  \hspace{1cm} (5)

where $P_{O_2}$ is the partial pressure of O$_2$, $p^\theta$ is the standard atmospheric pressure, and R is the universal gas constant. Due to the experiment being conducted in a vacuum, the practical pressure of oxygen is smaller than the total pressure of the vacuum chamber and certainly standard atmospheric pressure. This makes the value of $RT \ln \frac{P_{O_2}}{p^\theta}$ negative, i.e., the Gibbs free energy change of the reaction at T temperature is minor as compared with the standard Gibbs free energy change, making decomposition of the metal oxide easier to occur. On the other side, the equation shows that the decomposition temperatures of the metal oxide depend on the oxygen pressure. Thus, the vacuum degree was also the critical factor for the successful fabrication of Ti$_4$O$_7$ REM samples.

When $\Delta_r G = 0$, i.e., at the equilibrium, the relationship between temperature T and $\ln \frac{P_{O_2}}{p^\theta}$ was obtained:

$$\Delta_r G^\theta = -\frac{1}{2} RT \ln \frac{P_{O_2}}{p^\theta}.$$  \hspace{1cm} (6)

Based on the data of the Ti–O system, the diagram of this relationship is shown in Figure 10, called the Ti–O system phase stable diagram.

From Figure 10, Ti$_4$O$_7$ could be synthesized from TiO$_2$ if the oxygen partial pressure and temperature were accurately controlled. If the system oxygen partial pressure is higher than the equilibrium value, the metal will be oxidized, and if it is lower than the equilibrium value, then the oxide will be reduced. The lower the temperature was, the wider the range of the oxygen partial pressure for Ti$_4$O$_7$ existed.
fact, the last oxidized product is not TiO$_2$ but the mixture of various titanium oxide (Figure 11). As the temperature was 1273 K, the oxygen partial pressure $P_{O_2} = 10^{-18.6}$ MPa which is much lower than $10^{-7}$ MPa. The Ti powder used in our experiments is the nano-scale powder, which created a large surface area to contact with oxygen to increase the dissociation pressure of TiO$_2$ as much as possible kinetically.

4 CONCLUSION

In this study, the high purity Ti$_4$O$_7$ REM was successfully synthesized by mechanical pressing of TiO$_2$ powders followed by thermal reduction to Ti$_4$O$_7$ using the Ti powder as the reducing reagent. Carbon black was introduced to the monolithic TiO$_2$ precursor to control the pore size and morphology of the Ti$_4$O$_7$ REM. The pore properties modification increased the electroactive surface area by approximately 1.3-fold, which increased the reactivity of the Ti$_4$O$_7$ REM toward outer sphere electron transfer reactions. The electrodes had high porosities (38–59%), which showed high permeate fluxes of up to 1379 ± 8 LMH bar$^{-1}$. These results indicated that the Ti$_4$O$_7$ monolithic electrodes could find various electrochemical applications in water treatment and energy storage and conversion.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

GQ was responsible for conceptualization, investigation, formal analysis, and writing of the original draft. XW contributed to project administration, resources, validation, and reviewing and editing. JZ and CS carried out investigation and formal analysis, and writing of the original draft. XX helped with software and methodology. YZ, FR, and NZ performed the formal analysis and investigation.

REFERENCES

Bejan, D., Malcolm, J. D., Morrison, L., and Bunce, N. J. (2009). Mechanistic Investigation of the Conductive Ceramic Ebonex as an Anode Material. Electrochimica Acta 54 (23), 5548–5556. doi:10.1016/j.electacta.2009.04.057

Ganiyu, S. O., Otarun, N., Raffy, S., Cretin, M., Esmilaire, R., van Hullebusch, E., et al. (2016). Sub-stoichiometric Titanium Oxide (Ti4O7) as a Suitable Ceramic Anode for Electrooxidation of Organic Pollutants: A Case Study of Kinetics, Mineralization and Toxicity Assessment of Amoxicillin. Water Res. 106, 171–182. doi:10.1016/j.watres.2016.09.056

Geng, P., and Chen, G. (2016). Magnéli Ti 4 O 7 Modified Ceramic Membrane for Electrically-Assisted Filtration with Antifouling Property. J. Membr. Sci. 498, 302–314. doi:10.1016/j.memsci.2015.07.055

Graves, J. E., Pletcher, D., Clarke, R. L., and Walsh, F. C. (1991). The Electrochemistry of Magnéli Phase Titanium Oxide Ceramic Electrodes Part I. The Deposition and Properties of Metal Coatings. J. Appl. Electrochem. 21 (10), 848–857. doi:10.1007/bf01042450

Grimm, J., Bessarabov, D., and Sanderson, R. (1998). Review of Electro-Assisted Methods for Water Purification. Desalination 115 (3), 285–294. doi:10.1016/s0011-9164(98)00047-2

Guan, K., Qin, W., Liu, Y., Yin, X., Peng, C., Lv, M., et al. (2016). Evolution of Porosity, Pore Size and Permeate Flux of Ceramic Membranes during Sintering Process. J. Membr. Sci. 520, 166–175. doi:10.1016/j.memsci.2016.07.023

Guo, D., Shibuya, R., Akiba, C., Saji, S., Kondo, T., and Nakamura, J. (2016). Active Sites of Nitrogen-Doped Carbon Materials for Oxygen Reduction Reaction Clarified Using Model Catalysts. Science 351 (6271), 361–365. doi:10.1126/science.aad0832
