

Effect of CaTiO₃ Crystal Structure and Cathodic Morphological Structure on the Electrolysis

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TiO₂ and CaTiO₃ were electrolyzed in molten CaCl₂ to investigate the different electrochemical behaviours of *in situ* and *ex-situ* CaTiO₃ and the caused reason of the difference. The products were detected by X-ray diffraction, scanning electron microscope and BET specific surface area analyzer. It was shown that, electrolysis of *ex-situ* CaTiO₃ as starting material exhibited remarkable advantages for the crystal structure and morphological structure. *Ex-situ* CaTiO₃ has been deviated before the process, but the crystal distortion of *in situ* CaTiO₃ formed *via* TiO₂ is later than *ex-situ* CaTiO₃, lattice distortion is helpful for the removal of Ca²⁺ and O²⁻, which is good for the electrolysis of *ex-situ* CaTiO₃; the specific surface area of *ex-situ* CaTiO₃ is larger than *in situ* CaTiO₃ formed *via* TiO₂, which may promote the formation of more reactive sites; the porosity of *ex-situ* CaTiO₃ is larger than *in situ* CaTiO₃ formed *via* TiO₂, owning more and larger pore is favorable of ion migration.

Key Words: CaTiO₃, Crystal structure, Pore structure, Reactive sites.

INTRODUCTION

Titanium is widely used in aviation, civilian and industrial fields due to its being extraordinarily light weight and corrosion resistant. Although the demand for Ti is continuously growing in recent years, the imperfections in production technologies are limiting its applications.

Among the technologies proposed by researchers, FFC is representative of fused salt electrolysis process. Since it was proposed by Fray¹, FFC has been greatly developed and implemented in the preparation of metal and alloys²⁻⁶. The preparation of Ti by FFC was attracted widespread attention.

In the electrolysis of TiO₂ to obtain Ti, the presence of intermediate perovskite often gives rise to low productivity, when form low-valence titanium, intermediate perovskite also existed, then intermediate perovskite electrolyzed to Ti gradually⁷⁻¹⁴, which caused the reiterant of the process. Lang, Jiang, *et al.*, using preformed CaTiO₃ as cathode for electro-reduction, the result showed this process was significantly increased electrolysis speed and efficiency^{13,14}. But the reason why *ex-situ* CaTiO₃ may have an advantage over *in situ* CaTiO₃ for electro-reduction and *in situ* CaTiO₃ prevent to increase electrolysis speed and efficiency are not fully understood, based on the previous study of sintering condition, electrolytic voltage and atmosphere, this work use TiO₂ and CaTiO₃ as samples electrolyzed in molten CaCl₂ under a certain suitable sintering and electrolytic condition, through investigating the

electrochemical behaviours of *in situ* and *ex-situ* CaTiO₃, the difference between *in situ* and *ex-situ* CaTiO₃ and the superiority of *ex-situ* CaTiO₃ in electro-reduction were studied. The research into electrolysis of CaTiO₃ of different sources has provided an opportunity to improve efficiency right at the beginning of process by choosing suitable starting material and to learn how *in situ* CaTiO₃ influence the electrolysis of TiO₂.

From the point view of sources, perovskite is rich in titanium concentrates, high titanium slag and the mantle. Therefore, refining Ti from calcium titanium is an effective way of utilization resources. The work of refining Ti from CaTiO₃ electrolysis reduction is not only conducive to improving the efficiency of electrolysis, but can also be applied to the natural calcium titanium resources and perovskite minerals. It is significant for refining Ti from titanium concentrates, high titanium slag and using resources reasonable.

EXPERIMENTAL

Cathode preparation and sintering: CaTiO₃ and TiO₂ was purchased and used as received powder. It was first mixed with proper amount of adhesive before being molded into disc (20 mm × 6 mm) by axial mould pressing at 40 MPa. After standing at room temperature for 24 h, the discs underwent heat treatment in stove. The hearth of the stove was first heated up to 450 °C in 1 h. After keeping at 450 °C for 1 h, temperature of the hearth was raised once again to 850 °C within 1 h. The

disc was preserved for 2 h at 850 °C and cooled to room temperature in stove before being taken out for electrochemical experiments. *Ex-situ* CaTiO₃ (99.99 %) was supplied by Alfa Aesar and processed into disc as TiO₂ before being used as cathode.

Electrochemical experiments: Either CaTiO₃ or TiO₂ disc was connected to molybdenum rod and worked as cathode. Electrolysis was performed in molten CaCl₂ with graphite rod as anode under argon atmosphere as follows: (1) programmed temperature was first raised to 100 °C and held for 1 h before being raised to 300 °C and held for 2 h; (2) programmed temperature was raised to 850 °C at which pre-electrolysis proceeded for 2 h at 2.8 V; (3) the pre-electrolyzed disc and anode was immersed in molten CaCl₂ at 3.2 V and 900 °C for 1, 2, 4 and 6, (for TiO₂ disc, time was extended to 8 h); (4) when electrolysis was completed, the disc was taken out of the molten CaCl₂ to cool to room temperature in hearth under argon atmosphere before being characterized.

Products handling and detection: To protect the electrochemically reduced discs, post treatment was conducted with care. Briefly, discs were first ultrasonically cleaned in 0.01 M HCl solution. The acid cleaned discs were rinsed thoroughly with distilled water and then immersed in distilled water to remove the molten salt and other contaminants before being dried for detection. The phases composition of the discs were determined with X-ray diffraction (XRD-6000); the morphology microstructure and element contents were analyzed with SEM-EDS (TESCAN VEGAII MU); the specific surface area was measured with BET (ASPA-2010).

RESULTS AND DISCUSSION

Products comparison: Fig. 1(a,b) presents the X-ray diffraction spectrum of the electrochemically reduced CaTiO₃ and TiO₂ discs. It is worth noting that the sample of TiO₂ for XRD detection was taken from the surface while that of CaTiO₃ from the cross section. Table-1 shows the element contents of electrochemically reduced TiO₂ (surface) and CaTiO₃ for 1-6 h.

Fig. 1(a) shows the composition of *in situ* CaTiO₃ disc changed into Ti₂O at the 1 h, both Ti₂O and Ti₃O at the 2 h. At the 4 h, CaTiO₃ disc is completely converted into Ti and no change is found in the following-up 2 h treatment. Fig. 1(b) indicates that the surface composition of TiO₂ disc underwent the following sequential transformations during the electrolysis: CaTiO₃ at the 1 h, Ti₂O and CaTiO₃ at the 2 and 4 h, Ti₃O at the 6 h, respectively.

From Fig. 1(a,b), it can be seen, the product of *ex-situ* CaTiO₃ quenched after around 1 h is similar to the surface product of TiO₂ quenched after around 2-4 h, for a longer time, *in situ* CaTiO₃ is fully reduced to Ti while TiO₂ changes into lower-valent titanium oxide. Therefore, in this system of the electrolysis, TiO₂ may first need convert to *in situ* CaTiO₃, then further be reduced. However, the further electrolysis of *in situ* CaTiO₃ is fall behind *ex-situ* CaTiO₃, the de-oxidation effect of the product of TiO₂ quenched after around 4 h is not more fully than *ex-situ* CaTiO₃ quenched after around 1 h.

Table-1 shows that Ti wt % of the product of *in situ* CaTiO₃ and TiO₂ increased with longer electrolysis. Ti wt % of further electrolytic products of *in situ* CaTiO₃ formed *via* TiO₂ is

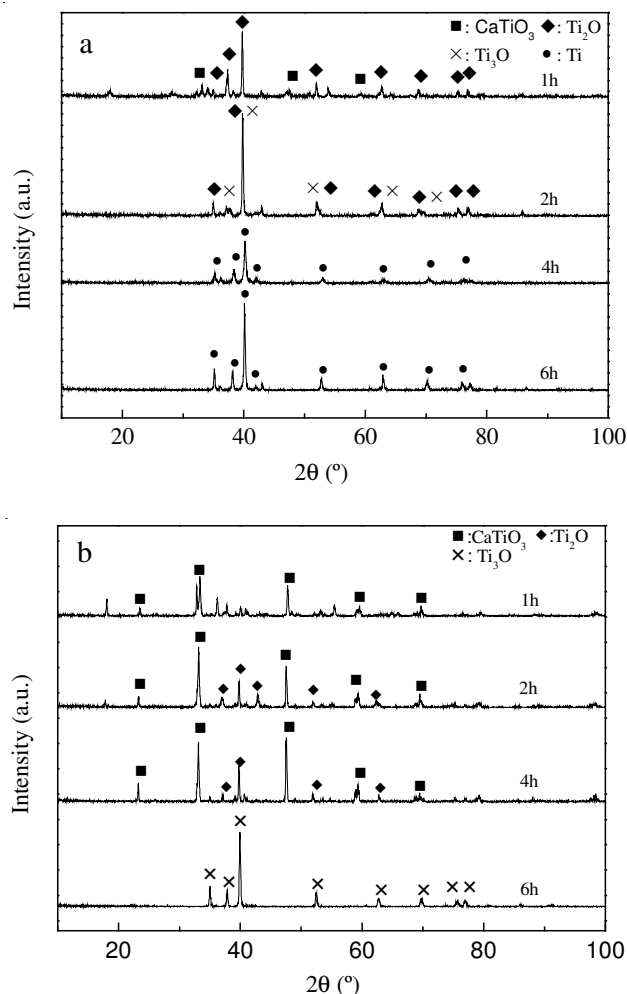


Fig. 1. XRD of TiO₂ (a) and CaTiO₃ (b) electrochemically reduced for 1-6 h

TABLE-1
ELEMENT CONTENTS OF TiO₂ (SURFACE) AND *EX-SITU*
CaTiO₃ ELECTROCHEMICALLY REDUCED FOR 1-6 h

Sample	Electrolytic time (h)	Ti (wt %)	O (wt %)	Other (wt %)
TiO ₂	1	35.11	34.54	30.35
	2	60.75	30.20	9.05
	4	62.31	27.89	9.8
	6	89.41	9.74	0.85
CaTiO ₃	1	65.34	25.01	9.65
	2	88.72	9.30	1.98
	4	96.21	—	3.79
	6	97.10	—	2.90

lower than *ex-situ* CaTiO₃ electrolyze in corresponding time. Ti wt % of the product of *in situ* CaTiO₃ formed *via* TiO₂ electrolyze in 3 h is similar to *ex-situ* CaTiO₃ electrolyze in 1 h.

The above results suggest that in the same condition, electrolysis with *ex-situ* CaTiO₃ as starting material exhibited remarkable advantages over *in situ* CaTiO₃ formed *via* TiO₂, this work would like to analyse differences of *in situ* and *ex-situ* CaTiO₃.

Effect of crystal structure on the removal of ions: The perfect CaTiO₃ unit cell is cubic structure defined with space lattice constants a, b and c. The actual a, b and c of CaTiO₃

unit cell in practice are usually deviated from the ideal values due to lattice distortion. In this work, *a*, *b* and *c* of CaTiO_3 at certain treatment stage were calculated with software Jade 5.0 as shown in Table-2. The ratio of *c* to *a*, c/a (≥ 1) was computed to evaluate the degree of lattice distortion. The higher is the value of c/a , the more the CaTiO_3 unit cell is distorted.

Sample	A (nm)	B (nm)	C (nm)	<i>c/a</i>
Sintered <i>ex-situ</i> CaTiO_3	0.5378	0.5444	0.7637	1.420045
CaTiO_3 generated from TiO_2 at 1 h	0.7600	0.7600	0.7600	1
CaTiO_3 generated from TiO_2 at 2 h	0.5378	0.5442	0.7640	1.420602
CaTiO_3 generated from TiO_2 at 4 h	0.5378	0.5444	0.7640	1.420602

The value of c/a which CaTiO_3 obtained from TiO_2 at 1st h is 1, indicating CaTiO_3 unit cell was cubic at the moment. At 2nd and 4th h, distortion of CaTiO_3 in TiO_2 disc is comparable to that of *ex-situ* CaTiO_3 disc. According to Madelung energy theory, attraction dominates the interactions existing among ions at lattices and Madelung energy increases when space lattice constants rise and *vice versa*¹⁵. Table-2 shows the space lattice constants, *a*, *b* and *c* of *in situ* CaTiO_3 in both TiO_2 disc at the 2nd and 4th treatment hour and *ex-situ* CaTiO_3 disc have decreased similarly and c/a increased indicating that Madelung energy has decreased and repulsion prevail.

Much work has been accomplished to highlight the effect of CaTiO_3 unit cell distortion. According to Wang¹⁶, unit cell distortion due to variation of Ti atomic location leads to significant transformation in the electronic structure of CaTiO_3 resulting reduced forbidden band, shrank energy gap between the conduction band and valence band. It has also been reported by Zhang *et al.*¹⁷ that, for perovskite (ABO_3), the dielectric constant ϵ and electron binding capacity will dwindle with the increase of c/a when c/a is greater than 1.0281. In this study, c/a values of CaTiO_3 in TiO_2 disc at the 2nd and 4th and in *ex-situ* CaTiO_3 disc are > 1.0281 due to unit cell distortion, which is favorable of the removal of Ca^{2+} and O^{2-} from perovskite.

In that sense, *ex-situ* CaTiO_3 has been deviated structure before the electrolysis and *in situ* CaTiO_3 formed via TiO_2 postpone the crystal distortion, lattice distortion is helpful for the removal of Ca^{2+} and O^{2-} , which is good for the electrolysis of *ex-situ* CaTiO_3 .

Effect of specific surface area on reactive sites: Table-3 shows the specific surface area of *ex-situ* and *in situ* CaTiO_3 . From Table-3, it can be seen, the sintered *ex-situ* CaTiO_3 is around 3 times larger than *in situ* CaTiO_3 formed from TiO_2 of 1 h electrolysis, *ex-situ* CaTiO_3 with larger specific surface area is favour to form more reactive sites.

Fig. 2 indicates schematically the tested sample locations with 'A' standing for the outer layer and 'B' standing for the inner layer. The XRD results of samples taken at 'A' and 'B' points from TiO_2 disc and CaTiO_3 disc after 8 and 4 h, respectively are shown in Figs. 3 and 4. The EDS results of samples

TABLE-3
SURFACE AREA OF *IN SITU* CaTiO_3 FORMED VIA TiO_2 OF 1 h TREATMENT AND SINTERED *EX-SITU* CaTiO_3

Sample	BET surface area ($\text{m}^2 \text{g}^{-1}$)
Sintered <i>ex-situ</i> CaTiO_3	1.5213
<i>In situ</i> CaTiO_3 formed via TiO_2 of 1h treatment	0.5096

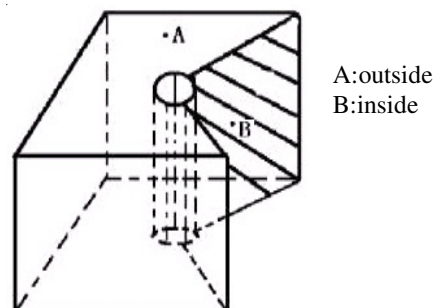


Fig. 2. Schematic diagram of the tested sample locations for XRD

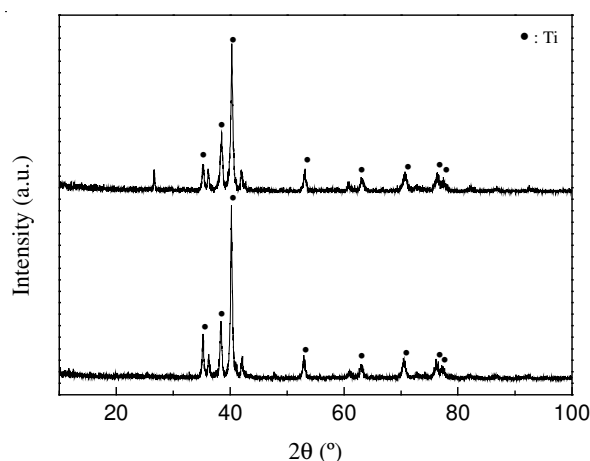


Fig. 3. XRD of samples at A and B of *ex-situ* CaTiO_3 after 4 h of treatment

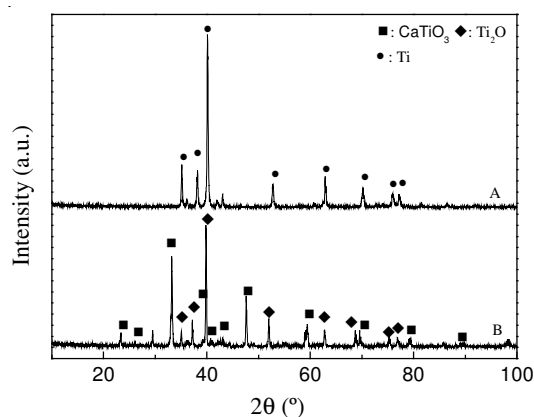


Fig. 4. XRD of samples at A and B of TiO_2 after 8 h of treatment

taken at 'A' and 'B' points from TiO_2 disc and CaTiO_3 disc after 8 and 4 h, respectively are shown in Figs. 5 and 6.

From Figs. 3-6, it can be seen, both the outer and inner products of *ex-situ* CaTiO_3 disc after 4h treatment are mainly metal Ti. On the other hand, after 8h treatment, the main component of TiO_2 disc surface is metal Ti and CaTiO_3 is still found in its inner region indicating that the desired reaction took place preferentially on the surface.

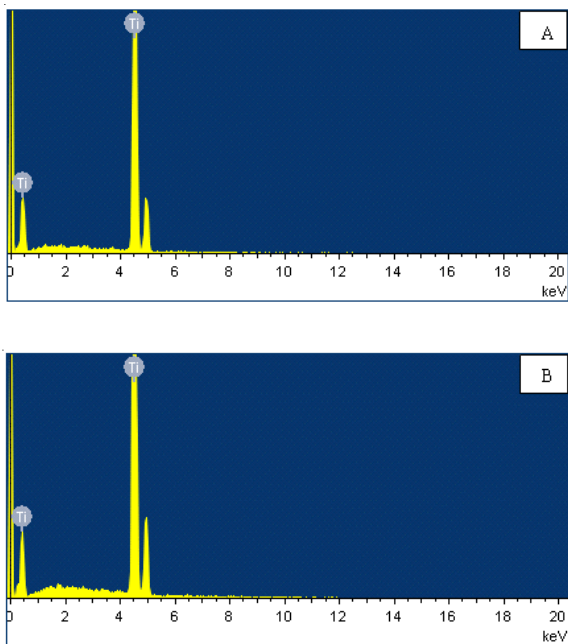


Fig. 5. EDS of samples at A and B of *ex-situ* CaTiO₃ after 4 h of treatment

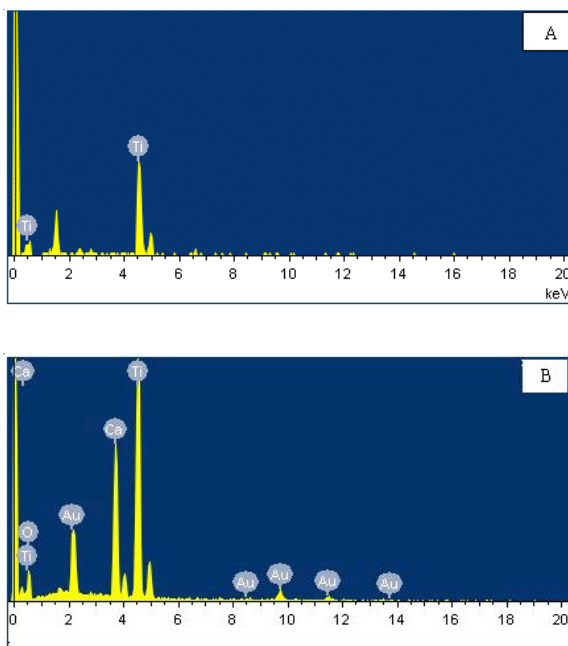


Fig. 6. EDS of samples at A and B of TiO₂ after 8 h of treatment

Fig. 7 is employed to schematically represent the crystal structure of CaTiO₃.

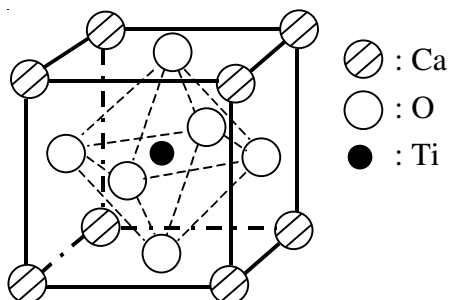


Fig. 7. Crystal configuration of CaTiO₃

From Fig. 7, it can be seen that in a CaTiO₃ unit cell, 6 oxygen atoms occupy the centers of its 6 crystal planes, 8 calcium atoms the 8 vertexes and 1 Ti atom the unit cell center. According to this unit cell structure, each oxygen atom is shared by two unit cells, 1 calcium atom belongs to 8 unit cells and only Ti is constrained in one unit cell. when CaTiO₃ changes into the target products, the removal of both Ca²⁺ and O²⁻ ions involved multiple unit cells.

The specific surface area usually refer to the appearance and pore inner surface area, for larger specific surface area may increase the interaction of ions and electrons and enhance the interaction, which enhance the ability of electron attachment, which is good for effective response area and thus enhance response activities, then form more crystals nuclear and multiple reactive sites. And multiple reactive sites is helpful for the share of unit cells. *Ex-situ* CaTiO₃ with larger specific surface area and reactive sites in inner and outer, cell connection is not limited to the outer layer, the overall reduction is faster. However, *in situ* CaTiO₃ with lower specific surface area and less reactive sites, cell connection of *in situ* CaTiO₃ is outer preference, the removal of CaTiO₃ may from outer to inner, internal CaTiO₃ may be delay to reduct and form sandwich instruction.

Therefore, specific surface area of *ex-situ* CaTiO₃ is larger than *in situ* CaTiO₃ formed *via* TiO₂, which is favour of forming more reactive site and the share of unit cells and the whole electrolysis is faster.

Effect of pore structure on ion migration: SEM of *ex-situ* CaTiO₃ and *in situ* CaTiO₃ formed *via* TiO₂ are shown in Figs. 8 and 9. Table-4 is the micropore volume of sintered *ex-situ* CaTiO₃ and *in situ* CaTiO₃ formed *via* TiO₂.

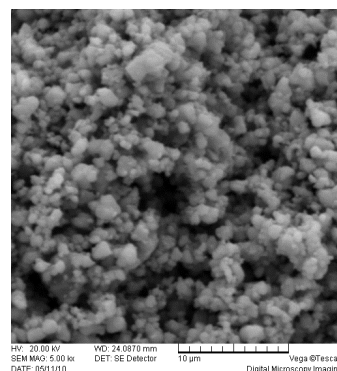


Fig. 8. SEM of sintered *ex-situ* CaTiO₃

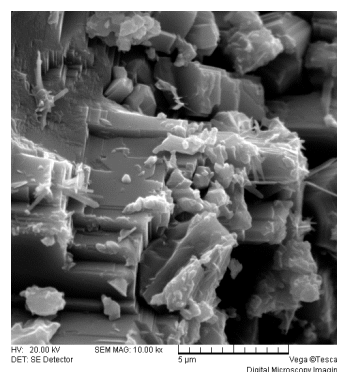


Fig. 9. SEM of *in situ* CaTiO₃ formed *via* TiO₂

TABLE-4
MICROPORE VOLUME OF SINTERED
EX-SITU CaTiO₃ AND IN SITU CaTiO₃ FORMED VIA TiO₂

Sample	Micropore volume (m ³ g ⁻¹)
Sintered <i>ex-situ</i> CaTiO ₃	0.000702
<i>In situ</i> CaTiO ₃ formed <i>via</i> TiO ₂ of 1 h treatment	0.000037

Ex-situ CaTiO₃ consisted of uniform small particles of fluffy structure as shown in Fig. 8, the structure is porous, which has a perfect pore alveolate structure with large amount of holes linking together, the pore diameter is *ca.* 3-5 μm, which helps the ion migration; in contrast, *in situ* CaTiO₃ is of dense bar flake structure with limited void space, internal the bulk is compact together, which is quite lack of pores and there is only cracks between bulks, thus cause the ion migration difficult. Table-4 shows that micropore volume of *ex-situ* CaTiO₃ is larger than *in situ* CaTiO₃ formed *via* TiO₂. The difference of the pore structure is dependent on environment and oriented crystal growth.

All the results suggest that *ex-situ* CaTiO₃ is more porous than *in situ* CaTiO₃ formed *via* TiO₂. Seen from Figs. 1(a,b), 3 and 4, both the outer and inner products of *ex-situ* CaTiO₃ after 4 h treatment are mainly metal Ti, but the surface of *in situ* CaTiO₃ after 5 h (*i.e.*, TiO₂ treated after 6 h) is still Ti₃O and there is difference of *in situ* CaTiO₃ after 7 h (*i.e.*, TiO₂ treated after 8 h). Which due to that more and larger pore structure is great benefit for ionic migration.

Therefore, *ex-situ* CaTiO₃ is more porous than *in situ* CaTiO₃ formed *via* TiO₂, which is helpful for ionic migration.

Conclusion

The advantages of *ex-situ* CaTiO₃ over *in situ* CaTiO₃ as starting material in electrochemical production of Ti is highlighted in view of crystal structure, pore structure and distribution of active sites: (1) *Ex-situ* CaTiO₃ was deviated structure, but the crystal of *in situ* CaTiO₃ formed *via* TiO₂ need experient crystal distortion, lattice distortion may reduce the bound of charge and is helpful for the remove of Ca²⁺ and O²⁻, which is good for *ex-situ* CaTiO₃; (2) the specific surface area of

ex-situ CaTiO₃ is larger than *in situ* CaTiO₃ formed *via* TiO₂, which may promote forming more reactive sites and the share of unit cells; (3) the porosity of *ex-situ* CaTiO₃ is larger than *in situ* CaTiO₃ formed *via* TiO₂, which makes *ex-situ* CaTiO₃ fully electro-deoxidation since well ion migration.

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