Simple and Efficient Fabrication of Mayenite Electrides from a Solution-Derived Precursor

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Supporting Information

ABSTRACT: Mayenite (12CaO-7Al2O3, C12A7) electride with an anti-zeolite nanoporous structure has attracted intense attention due to its versatile promising application potentials. However, the synthesis difficulty because of extremely harsh conditions (e.g., reduction in sealed calcium or titanium vapor) significantly obstructs its realistic applications. In this work, we employed a simple, efficient, and cost-effective route for synthesizing mayenite electrides (C12A7:e−) in both powder and dense ceramic. C12A7:e− powders with efficient electron doping (3.5 × 1020 cm−3) were obtained via simple graphite reduction of a novel mixture precursor of CaAl2O4 (CA) and Ca3Al2O6 (C3A) derived from a modified Pechini method. The structural evolution during the electride formation was investigated, and it was found that reduction below 1300 °C induced the formation of Ca3Al2O6 (C3A3), while reduction above 1400 °C helped retain the mayenite structure. Fully dense C12A7:e− ceramics were also fabricated via graphite reduction of presintered pellets with a relative density of 97.9% starting from the CA+C3A mixture. Careful studies improved the mechanism recognition of graphite treatment that the electrons injection was probably initiated by surface reduction with involatile C species (e.g., C2) rather than previously proposed CO, during which the mixed conduction of oxygen ions and electrons played an important role. Furthermore, the stability of C12A7:e− in water as well as in the presence of moisture was discussed. These results not only suggest a novel precursor for fabricating high-quality mayenite electrides but also provide in-depth insights into the stability of the mayenite structure toward practical applications.

1. INTRODUCTION

Recent years have seen increasing interest in electrides, being promising candidates in various fields, such as catalysis, batteries, and electronic and optoelectronic devices.4−6 Essentially, electride is a kind of ionic compounds in which each electron occupies one crystallographic site and acts as an anion.7 Due to the insufficient thermal and chemical stability of organic electrides at room temperature (RT), during the past decade, substantial efforts have been devoted to exploring inorganic substitutes.4,6,10−13 Among these inorganic electrides, C12A7:e− (Ca2Al2O3), derived from the substitution of clathrated oxygen ions by electrons in nanoporous mayenite (Ca12Al14O33, C12A7−O2−) structure, has been demonstrated to be the most promising one since the early 2000s.7−10 The characteristic chemical and electronic properties of C12A7:e− are mostly inherited from the special nanocaged structure of the electrons host (i.e., C12A7), which per unit cell consists of one positively charged lattice framework (Ca24Al28O644+) containing 12 sub-nanometer cages and four clathrated electrons (e−) randomly accommodated in 4 out of 12 cages. For the present, C12A7:e− has shown great potential in various applications, especially for catalytic ammonia (NH3) synthesis and decomposition,12,21−26 electron field emitters,16 and transparent conductive oxide (TCO).27−29 Obviously, according to specific applications, direct and simple preparation of powders as well as dense ceramics or thin films of C12A7:e− is of important significance.

In order to facilitate the evolution of C12A7:e− from C12A7−O2−, the Hosono’s group and several other groups have made great advances. So far, several strategies have been employed, mainly including (i) Ca vapor treatment under low pressures,9 (ii) hydrogen gas treatment, followed by UV irradiation,5,30 (iii) melt-solidification and glass-ceramics process,14,16 (iv) thermal treatment in reducing atmosphere,15 and (v) hot Ar+ ion implantation.31 Nearly all proposed methods required the use of additional metals (e.g., Ca, V, Ti),1,5,12,13,32 vacuum heat treatment,12,13,32 special encapsulation,9,13,14 and sometimes even using a single mayenite single crystal as precursor,9,5,32 and thus greatly hinder the direct and simple acquisition of C12A7:e− in desirable forms. Furthermore, there still exist controversies in the formation of C12A7:e− such as the stability of the mayenite structure during its high temperature (HT) evolution. For instance, Palacios et al. found that C12A7 decomposed at 1100 °C in reducing conditions to give Ca3Al2O6 (C3A) and Ca5Al6O14 (C5A).12

Received: June 28, 2017
Published: September 19, 2017
Similar instability of mayenite in a dry atmosphere was also mentioned in another work, in which OH⁻ was proposed to present a significant stabilization effect. 33 However, pure C12A7:e⁻ electrode has been repeatedly claimed after reduction at 1000–1600 °C without structural transition. 9,13–15 In addition, the stability of C12A7:e⁻ in aqueous solution as well as in the presence of moisture is of great importance for practical applications, which however has not been thoroughly discussed yet.

In this work, two CaO-Al₂O₃ precursors including a CA+C3A mixture and pure C12A7 were obtained via a modified Pechini method by simply adjusting the calcination temperature in air. Mayenite electrodes (C12A7:e⁻) in the form of both powders and dense ceramics were fabricated via one-step graphite reduction using the CA+C3A precursor. Compared to the commonly used C12A7 which resulted in an electron concentration of 2.4 × 10²⁰ cm⁻³, the precursor of CA+C3A mixture rendered more efficient electrons doping (3.5 × 10²⁰ cm⁻³) in as-reduced C12A7:e⁻. Careful studies indicated the nature of graphite reduction that the electrons injection was initiated by surface reaction with involatile C species (e.g., C₂⁻) rather than previously proposed CO. The mixed conduction of free oxygen ions (O²⁻) and electrons (e⁻) played an important role. The structural evolution during the high temperature reduction was also discussed. Furthermore, the stability of C12A7:e⁻ electrodes in water as well as in the presence of moisture was investigated.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Characterization. Calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O, 99%), aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, 98%), ethylene diamine tetraacetic acid (EDTA, 99.4%), citric acid monohydrate (C₆H₈O₇·H₂O, 99.5%), and ammonium hydroxide (NH₃·H₂O, 28%) are used as received from Alfa-Aesar without further purification. After complete dissolution of powders, the amount of residual I₂ was titrated using sodium thiosulfate (Na₂S₂O₃) solution (10⁻¹ M). Determination of the titration end point was enhanced by adding several drops of starch solution (0.1 wt %).

2.2. Synthesis of CaO-Al₂O₃ Precursors. Various precursors were prepared via a modified Pechini method. 34,35 Briefly, stoichiometric Ca(NO₃)₂·4H₂O and Al(NO₃)₃·9H₂O (12:14) were dispersed into an aqueous solution of EDTA and citric acid with continuous stirring at room temperature. The molar ratio among EDTA, citric acid, and metal ions is 1.5:1:1. Afterward, ammonium hydroxide (NH₃·H₂O) was slowly added in the above slurry until the formation of a clear solution. After the evaporation of water, a claybank gel was obtained, which was then put into a drying oven at 150 °C for 48 h to get the charcoal-like powders. A mixture of CaAl₂O₄ (CA) and Ca₄Al₂O₆ (C₃A) can be obtained via calcining the charcoal-like powders in air at 950 °C for 10 h led to the formation of a mixture of CaAl₂O₄ (CA) and Ca₄Al₂O₆ (C₃A). With the increase of temperature above 950 °C, Ca₁₂Al₁₄O₃₃ (C12A7) appeared and gradually increased until the formation of pure mayenite at 1200 °C, which can be clearly traced by the intensity of the (211) diffraction peak at 18.12°. Besides, the evolution of C12A7 was accompanied by the formation and elimination of CaO and Al₂O₃ phases. It was once reported by Kim et al. that C₃A+CA eutectic formed from C12A7.

2.3. Preparation of C12A7 Dense Ceramics. Powders of the CA+C3A mixture (0.2–0.5 g) were pressed into disks using a Fl-13 mm die under a uniaxial pressure of 100 MPa. Afterward, the green pellets on top of alumina substrates were sintered at 1200–1300 °C for 10 h in air, with a ramp of 2 °C min⁻¹, which allowed us to achieve a flat surface of the sinters without cracks. Finally, sintered disks were polished to remove the surface layer for further treatment and characterisation. The bulk densities of the sintered disks were measured by the Archimedes method, using kerosene as medium. As a comparison, sintered ceramic disks were also obtained directly from crystalline C12A7 powders.

2.4. Synthesis of Mayenite Electrides. C12A7:e⁻ in forms of powder as well as dense ceramics was obtained via simple graphite reduction from the CA+C3A precursor. Powdered electrides were prepared by directly heating the CA+C3A precursor powders in a tubular graphite crucible at 1200–1450 °C for 3–12 h under a dry Ar gas flow. Dense C12A7:e⁻ ceramics were obtained by heating presintered C12A7 disks buried in graphite powders (Alfa-Aesar, 300 meshes) under the same conditions. The above heat treatments were conducted on a horizontal tube furnace.

2.5. Determination of Electrons Concentration. The electron injections in as-prepared C12A7:e⁻ powders starting from both the CA+C3A mixture and crystalline C12A7 were evaluated via the iodometry method. 39 Briefly, 20 mg of electrode powders was dispersed in aqueous iodine (I₂) solution (5 mL, 10⁻³ M). The pH was adjusted to 0.5 with addition of HCl (2 M). The mixture was kept at 20 °C in the dark and sealed to prevent the reoxidation of I⁻ ions. After complete dissolution of powders, the amount of residual I₂ was titrated using sodium thiosulfate (Na₂S₂O₃) solution (10⁻³ M). Determination of the titration end point was enhanced by adding several drops of starch solution (0.1 wt %).

3. RESULTS AND DISCUSSION

3.1. Synthesis of CaO-Al₂O₃ Precursors. The charcoal-like powders derived from the modified Pechini process were calcined at different temperatures in air to obtain CaO-Al₂O₃ precursors for preparing mayenite electrides (C12A7:e⁻). The crystallographic structure and phase composition of as-calcined powders were characterized by X-ray diffraction (XRD). As shown in Figure 1, 950 °C calcination for 10 h led to the
decomposition during the solidification of a reduced C12A7 melt at 1600 °C, which has been ascribed to the absence of template anions in the cages.14,16 Herein, we obtained the powder mixture of CA and C3A directly from the metal-ions-containing precursor in atmospheric air at much lower temperature. The exact mechanism is still under in-depth discussion, while the locally reducing environment produced by combustion of the carbonaceous precursor might play an important role. The CA+C3A mixture and the phase-pure C12A7 were further investigated for morphologies and microstructure via scanning electron microscope (SEM). As shown in Figure 2a, the CA+C3A mixture presents particle aggregates (2–4 μm) together with separate particles (~300 nm), probably indicating the coexistence of two crystalline phases. Pure C12A7 (Figure 2b) presents a random stacking of particles (~500 nm) with partial fusion, suggesting grain growth during the phase transition. The specific surface areas were decided to be 7.81 and 5.40 m² g⁻¹ for the CA+C3A mixture and pure C12A7, respectively. In contrast, pure C12A7 was also prepared via direct solid state reaction (C12A7-SSR) between CaCO₃ and γ-Al₂O₃. As shown in Figure S1, C12A7-SSR presents obvious sintering of grains of 2–8 μm, in accordance with the low BET surface area of less than 1 m² g⁻¹.

3.2. Preparing Mayenite Electride (C12A7:e⁻) Powders. In order to obtain C12A7:e⁻ powders, we employed high temperature (HT) treatment in a graphite environment, which was proposed to easily produce an effective reducing atmosphere (e.g., CO).15 The CA+C3A mixture as powder precursor was treated in a graphite crucible at elevated atmosphere (e.g., CO).15 The CA+C3A mixture and the phase-pure C12A7 were prepared in a graphite crucible at elevated temperature. The mayenite crystal structure did not form until 1400 °C, below which the resulting powders presented C₆₃Al₆O₁₄ (CSA3) as the main phase. Palacios et al. once reported the C12A7 decomposition into CSA3 and C3A at 1100 °C under dry reducing conditions and proposed that the mayenite structure was not stable in the absence of any template cage ions (e.g., O²⁻, OH⁻, F⁻).12 This explanation also applies to our results, which however were not observed after similar treatment in a carbon crucible in another work.15 After being reduced at 1400 °C, the product presented a pure mayenite structure as well as a black green coloration, indicating the formation of C12A7:e⁻ electrocatalysts.5,12,14,15,36 The specific surface area was decided to be 2.41 m² g⁻¹. However, further increasing the temperature to 1450 °C induced the appearance of CS3A, though the mayenite structure was mostly retained. Besides, as shown in the insets (Figure 3), the white powders of the CA+C3A mixture changed to a totally black solid, which should be due to the in situ electride formation during the melt and resolidification.14,16

In order to study the influence of precursors on electride formation, the pure C12A7 powders were taken for comparison, which have been commonly used for preparing mayenite electrides. As shown in Figure S2, compared to the CA+C3A mixture, starting from pure C12A7 presented an identical phase evolution with the increase of reduction temperature. However, an obvious color difference was observed among samples derived from different precursors, suggesting different levels of electrons injection into the cage-like C12A7 structure.17,22 As shown in Figure 4, various samples present an obvious difference in the light absorption in the UV–vis (5.5–1.2 eV) range. Pristine C12A7 shows white color and presents negligible absorption in the visible range (1.6–3.2 eV). After 1200 °C reduction, the CSA3-based powders starting from C12A7 are still white, while a gray coloration is presented when starting from the precursor powder of CA+C3A, probably arising from the crystal defects (e.g., oxygen vacancies) introduced by the high temperature reduction.37–39 Notably, after reduction at 1400 °C, powders derived from pure C12A7 and CA+C3A precursors both present obvious green coloration, along with the appearance of a new absorption band located around 2.8 eV. For C12A7:e⁻,

Figure 2. Scanning electron microscope (SEM) images of CA+C3A mixture (a) and pure phase C12A7 powders (b).

Figure 3. X-ray diffraction (XRD) patterns of the powder precursor of CA+C3A after reduction in graphite crucible at different temperatures, along with digital pictures of powder samples.
this absorption is attributed to an intracage s-to-p transition of trapped electrons, and can be used to precisely evaluate the concentration of electrons which is proportional to its intensity.\textsuperscript{17,40,41} Obviously in Figure 4, the CA+C3A derived sample presents much darker coloration compared to the counterpart from pure C12A7. That is, the CA+C3A mixture as precursor can help make C12A7:e\textsuperscript{−} with a higher concentration of electrons, greatly favorable for enhanced catalytic and conductive properties.\textsuperscript{9,22} The accurate electron concentration of various samples was further evaluated via the iodometry method, as described previously.\textsuperscript{29} With the reduction at 1400 °C for 6 h, the electron concentration in C12A7:e\textsuperscript{−} powders starting from the CA+C3A mixture was about 3.5 × 10\textsuperscript{20} cm\textsuperscript{−3}, while the concentration is only 2.4 × 10\textsuperscript{20} cm\textsuperscript{−3} for powders from crystalline C12A7, clearly confirming the above inference from the absorption spectra in Figure 4.

3.3. Preparing Mayenite Electride (C12A7:e\textsuperscript{−}) Dense Ceramics. For applications involving ionic or electronic conduction, dense ceramics are highly desirable. Obviously, the dense ceramic of C12A7 is a prerequisite for making a dense ceramic of C12A7:e\textsuperscript{−} electrode. In order to facilitate the densification process of C12A7, researchers have employed several methods and achieved reasonable success, such as the spark plasma sintering (SPS).\textsuperscript{32–35} Herein, we tried to make dense C12A7 ceramics from the precursor powders of the CA +C3A mixture and pure C12A7. As indicated in Figure S3a, after sintering at 1200 °C for 10 h, the pellet starting from C12A7 presented distinct porosity. Increasing the temperature to 1300 °C (Figure S3b) slightly improved the situation, which is still far from satisfied. Notably, using the CA+C3A mixture as starting powders for green pellets did make a difference. As shown in Figure S3c, significant reduction of porosity was observed after sintering at 1200 °C. Sintering at 1300 °C further enhanced the densification (Figure S3d), making a density of 2.621 g cm\textsuperscript{−3}, 97.9% of the theoretical density (2.676 g cm\textsuperscript{−3}). We believe the densification can be further enhanced by increasing the grain size or pressure and optimizing the sintering process, which however is not the key concern in this work.

The simple graphite reduction was also applied to the above sintered C12A7 pellets for making dense C12A7:e\textsuperscript{−} ceramics. Briefly, the dense C12A7 disks were buried in graphite powders (Alfa-Aesar, 300 meshes) and then subjected to heating in dry Ar at different temperatures. Similarly, the instability of the mayenite crystal structure in dry reducing conditions at 1200 °C was confirmed. As indicated in Figure S4, after 6 h reduction, there appeared clear peaks indexed to C5A3 among the diffraction peaks of C12A7. Compared to that in powders, the slower phase transition within the sintered pellet probably originated from the slow removal of template O\textsuperscript{2−} due to its long diffusion distance from the bulk to the surface. Notably, after 6 h reduction at 1400 °C, the white C12A7 pellet turned to be nearly black, indicating the formation of electride, as shown in Figure 5a. Besides, the cross-sectional SEM images (Figure 6a) indicated that the densification of sintered C12A7 ceramics was not degraded by the extraction of cage O\textsuperscript{2−} ions during graphite reduction. In contrast, much lower density with many closed pores (Figure 6b) was observed in graphite-reduced C12A7 pellets sintered from pure C12A7, clearly indicating the priority of using the CA+C3A mixture as the precursor for making dense C12A7:e\textsuperscript{−} ceramics. More detailed discussion on the formation of C12A7:e\textsuperscript{−} from powders as well as dense ceramics will be presented in the following section.

3.4. Formation Mechanism of C12A7:e\textsuperscript{−} Electride. It is reasonable to ascribe the electride formation to continuous extraction of free O\textsuperscript{2−} ions by reductive species, such as the Ca vapor and CO gas, leaving electrons behind in the cages. Several studies proposed that higher levels of electron doping can be achieved via simply prolonging the reduction duration.\textsuperscript{9,36} In this study as shown in Figure S5, with the increase of reduction time from 3 to 12 h, the crystal structure of resulting powders kept identical. Diffuse reflection spectra (DRS) were used to evaluate the electrons injection effect. As indicated in Figure S6, the intensity of absorption bands at 2.8 eV was nearly the same for powders reduced at 1400 °C for different durations. A similar phenomenon was also observed for the graphite reduction of dense C12A7 pellets (Figure S7a).

As indicated by the surface as well as the cross-sectional views

![Figure 4](image-url) Diffuse reflection spectra (DRS) of the CA+C3A mixture and pure C12A7 powders after graphite reduction. Insets are digital pictures of samples and schematic diagram of the electronic structures of C12A7 and C12A7:e\textsuperscript{−}. FCB and FVB are framework conduction band and framework valence band, respectively. CCB represents the cage conduction band arising from three-dimensionally connected cages.

![Figure 5](image-url) (a) Digital pictures of dense C12A7 pellets before and after graphite reduction at 1400 °C for 6 h. (b) A schematic diagram of the heat treatment using a tube furnace. (c) Digital pictures of C12A7 powders within a covered alumina crucible before and after the heat treatment in dry Ar gas at 1400 °C for 6 h.
of the reduced disks with different thickness, the electron distribution is quite homogeneous throughout the dense electride ceramics. Therefore, it seems that extraction of free $O^{2-}$ is not the apparent rate-determining step (RDS) during the electrode formation within a hours’ scale. It has also been proposed that removal of clathrated hydroxyls (OH$^-$) inevitable in air-calcinated mayenite is a prerequisite for introducing high-density anions into the cages, such as H$^+$ and O$^{2-}$. However, herein, no matter if the precursor powders had been dehydrated in dry air above 1000 °C prior to the graphite reduction, no difference can be observed in the prepared electrides, as confirmed in Figures S5 and S6.

It was proposed that the strongly reducing CO/CO$_2$ atmosphere inside the carbon crucible is the key species during the formation of C12A7:$e^-$ electride at high temperatures (1000–1200 °C). It has also been suggested by the same research group that C$_2^{2-}$ ions can dissolve into the C12A7 melt at 1600 °C from the carbon crucible to compensate the removal of clathrated oxygen. Herein, a controlled experiment was conducted to get further insights into the electrode formation. On the one hand, as indicated in Figure 5b, C12A7 powders and a graphite block were separately located in a covered alumina crucible, which was then subjected to 1400 °C 12A7 powders and a graphite block were separately located in a covered alumina crucible, which was then subjected to 1400 °C heating for 6 h within a dry Ar flow. However, after the above process, C12A7 powders changed from white to black (Figure 5c) rather than green or black, indicating insufficient electrons injection. A similar phenomenon was also observed for dense C12A7 ceramics that reduction in a covered graphite crucible only rendered flaxen coloration to white pellets (Figure S7b), suggesting that gas molecules such as CO might not be the key reducing agent. Furthermore, CO of proposed concentration (>0.99 atm) was not easy to be achieved in the inert Ar atmosphere. On the other hand, the melting point of C$_2$ is nearly impossible without the fast interstitialcy exchange between framework and cage anions, which is the origin of the high oxygen ion conductivity in the mayenite structure at elevated temperatures. That is, the C$_2^{2-}$ involved reduction should be limited to surface reactions.

Given the above discussion, we proposed a reasonable explanation for the formation of C12A7:$e^-$ electrode, as indicated in the schematic diagram (Figure 7). First, with the activation of high temperatures, highly reducing C species (e.g., C$_2^{2-}$) will react with free oxygen (i.e., cage O$^{2-}$) in the surface layer of C12A7, producing CO/CO$_2$ in the environment. Surface removal of one cage O$^{2-}$ ion is accompanied by the back injection of two electrons into the cages. Meanwhile, the mayenite structure is essentially a mixed ionic and electronic conductor (MIEC) at elevated temperatures until the formation of pure C12A7:$e^-$ with 100% electrons doping. Therefore, the above surface process can be efficiently facilitated by the continuous transport of cage oxygen from the bulk to the surface as well as the reversed diffusion of injected electrons from the surface to the bulk. Given that the final concentration of electrons in the electrode was deemed to be governed by the reduction temperatures rather than the durations, the formation of C12A7:$e^-$ electrode is more like a thermodynamics-controlled process, but not a dynamics-controlled one. As for the verified priority of starting from the CA+C3A mixture for higher electrons doping in section 3.2, it can be reasonably attributed to the simultaneous injection of electrons along with in situ formation of the cage framework in the mayenite electride.

3.5. Room-Temperature Stability of C12A7:$e^-$ Electride. For practical uses, understanding the stability of C12A7:$e^-$ electrode in water as well as in the presence of moisture is of great importance. It was occasionally mentioned that Ru/C12A7:$e^-$ showed degraded catalytic activity once water is absorbed, but no detailed description has ever been provided. In this work, we carefully studied the stability of both powders and dense ceramics of C12A7:$e^-$ electrides synthesized from CA+C3A precursor in aqueous solution as well as 100% relative humidity, as shown in Figure S8.

For C12A7:$e^-$ powders as shown in Figure 8, after being immersed in water for 24 h, the black green electride turned...
purely white. The XRD pattern indicated that C12A7:e− easily reacted with water and changed to Ca3Al2(OH)12 with a slight amount of Al(OH)3. The phase transition can be confirmed via SEM investigation (Figure S9) that large grains (2−4 μm) in the electride decomposed into flake-like fragments in the hydroxide. The above hydration process was also detected after being stored in air with 100% relative humidity for 1 week. As indicated by the insets of Figure 8, C12A7:e− presented the color degradation from black green to bright green, along with the particles forming a monolith with a certain strength. This phenomenon suggested that the electron concentration within the powders decreased, in accordance with the XRD data that there appeared Ca3Al2(OH)12 as impurity phase. For C12A7:e− dense ceramics, similar results were obtained. As shown in Figures 9 and S10, after being immersed in water for 4 days, there appeared a rough layer due to the formation of lamellar hydroxide on the surface, as confirmed by the XRD results in Figure S11.

The above results indicate the instability of C12A7:e− electrode in the presence of H2O molecules, though it seems that the structural degradation is much slower for dense ceramics in moisture than that for powders in aqueous solution. This water sensitivity should be taken into serious consideration when confronting with H2O containing applications. Separating materials may be useful when C12A7:e− electrodes are involved in a H2O containing environment, such as the utilization of polymeric and ceramic membranes in electrochemical devices.

4. CONCLUSIONS
In summary, a CA+C3A mixture and pure C12A7 powders were obtained by calcining the charcoal-like powders derived from a modified Pechini process at different temperatures and were used as precursors for the synthesis of mayenite electrides (C12A7:e−). Formation of C12A7:e− powders via one-step graphite reduction was studied using the above CaO-Al2O3 precursors. The precursor powder of the CA+C3A mixture presented obvious priority to the commonly used C12A7 in fabricating C12A7:e− with much higher levels of electrons doping (3.5 × 1020 cm−3). Furthermore, the CA+C3A mixture resulted in much denser ceramics of C12A7 with a relative density of up to 97.9% compared to pure C12A7 powders as the precursor, which were further reduced into fully dense C12A7:e− pellets. Control experiments unveiled the nature of graphite reduction that the electrons injection was initiated by surface reaction with involatile C species (e.g., C2−) rather than CO. During the electride formation, the mixed conduction of cage oxygen ions (O2−) and doped electrons (e−) played an important role. Moreover, the structural stability of C12A7:e− powders and dense ceramics during high-temperature graphite reduction as well as in the presence of H2O molecules was discussed in detail. With no doubt, these results provide more comprehensive insights into the fabrication of high-quality mayenite electrides toward practical applications.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b01655.

Figure 8. X-ray diffraction (XRD) patterns of C12A7:e− electrode powders before and after being immersed in deionized water for 24 h, as well as being stored in a glass bottle with a 100% relative humidity for 1 week. Insets are the digital pictures of samples.

Figure 9. Cross-sectional (a) and top (b) SEM views of C12A7:e− pellet after being immersed in deionized water for 4 days.

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The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b01655.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge the financial support from the startup fund of Clemson University.

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