Synthesis, Reduction, and Electrical Properties of Macroporous Monolithic Mayenite Electrides with High Porosity

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ABSTRACT: Room-temperature stable macroporous mayenite electride (C12A7:e−) has been successfully prepared via a sol–gel method accompanied by phase separation, followed by heat-treatment and reduction processes. The obtained xerogel monoliths possess controllable macrostructure and a porosity of more than 60%, depending on adjusting the amount of poly(ethylene oxide) as a phase separation inducer. Heat-treatment allows the formation of multicrystals Ca12Al14O32Cl2 and Ca12Al14O33 (C12A7), and the porosity increases to 78.67% after being heat-treated at 1100 °C. Further reduction promotes the transformation from Ca12Al14O32Cl2 or C12A7 to C12A7:e− as well as the conversion from an insulator to a semiconductive electride. The carrier concentration of the electride reaches 3.029 × 1018 cm−3 after being reduced at 1100 °C under Ar atmosphere, and the porosity still remains 66%. The macrostructure of the resultant mayenite electride before and after heat-treatment and reduction is perfectly preserved, indicating that the obtained macroporous monolithic mayenite electride could be utilized in the electronic components.

INTRODUCTION

An electride, in which the electrons act as anions in the compounds, is a kind of a special crystalline ionic material. In 1990, two kinds of electrides (Cs+(18-crown-6)2e− and K+(crtystal[2.2.2])2e−) have been synthesized by James L. Dye. Different from the metals, the electrons in electrides are usually not absolutely delocalized and cannot be thought of as a “sea of electrons”. At present, the inefficient control over the consistence of the electron anions and the low thermal stability are the main limitations of the electrides required to improve. Mayenite (Ca12Al14O33, that is, 12CaO·7Al2O3, C12A7), a complex binary oxide material, can be converted to a novel electride from an insulator because of its stable structure in room-temperature and high carrier concentration. The unique properties of C12A7 come from its special “cage” structure with inner diameters of approximately 0.5 nm. Two extra O2− ions (generally known as free oxygen ions) take over 2 out of 12 cages in a unit-cell. The C12A7 can be reduced so that part of the free oxygen ions can be substituted by the equivalent number of extra framework electrons, which makes C12A7 a room-temperature stable electride.

C12A7 was first found in the cement in 1936 and after some years, the space group of C12A7 has been announced through the analysis of its single crystal X-ray diffraction (XRD) data that its space group was finally stated and further verified by neutron powder diffraction data. The fabrication of the first inorganic electride stable at room-temperature in air was reported by Matsuishi et al., and they confirmed the electride form of C12A7 with electron paramagnetic resonance spectroscopy. Kim et al. reported two additional synthetic methods more simply and directly adapted for large scale preparation of a kind of polycrystalline C12A7 electride through the concretion of the stoichiometric C12A7 melt under a reducing atmosphere. Matsuishi et al. also introduced a direct synthesis method for the fabrication of C12A7 electride powder. Rand et al. described the efforts to fabricate and test a hollow cathode that utilizes C12A7 electride as a thermionic emission surface.

Up to now, a number of techniques have been utilized for the fabrication of C12A7 materials. However, there have been few reports about porous C12A7 with interconnected macropores and co-continuous skeletons, except for our previous work. The space of the macropores allows the chemical reactions to act thoroughly and reduces the resistance of the liquid flow. Such a stable conductive material with macropores inside can be applied to a series of areas, such as a porous electrode, the carrier of catalyst for some electrochemical reaction, and so on.

In this work, we report the preparation of macroporous monolithic mayenite electride via the sol–gel method
accompanied by phase separation, followed by heat-treatment and further reduction. During reduction, the free oxygen ions in the special cage structure of mayenite are replaced by electrons to obtain special room-temperature stable mayenite electrides (C12A7:e\(^{-}\)). The macrostructure formation, heat-treatment, and reduction of the resultant macroporous monolithic mayenite electrides are investigated in detail. The crystal structures of the C12A7 before and after reduction are also calculated by the CAmbridge Serial Total Energy Package (CASTEP) code.

**RESULTS AND DISCUSSION**

In our approach, the calcium chloride dihydrate (CaCl\(_2\)·2H\(_2\)O) and aluminum chloride hexahydrate (AlCl\(_3\)·6H\(_2\)O) were used as ionic precursors, and a chelating agent glycol (EG) was used to restrain the precipitation of Ca\(^{2+}\) ions. The poly(ethylene oxide) (PEO) promotes the phase separation of the system, and the propylene oxide (PO) accelerates the sol–gel transition so that the macrostructure will be frozen during phase separation. The shrinkage and crack of gels during drying can be prevented through the addition of formamide to reduce the capillary pressure during drying. A schematic diagram of the sol–gel process accompanied by phase separation of the Ca–Al–O system has been shown in Figure S1. Figure 1 depicts the appearance of morphologies of dried gel synthesis with different W\(_{\text{PEO}}\). All of the dried gel samples exhibit a 3D network structure, in which both co-continuous skeletons and interconnected macropores simultaneously exist in the macrostructure. With the increase of W\(_{\text{PEO}}\), the 3D network structure does not change a lot before the W\(_{\text{PEO}}\) reaches 0.24 g, whereas the macropore size of the as-dried samples decreases obviously. The scanning electron microscopy (SEM) image of the mayenite samples in different magnifications for sample B has been shown in Figure S2. When 0.24 g of PEO is added, the particle aggregates will be obtained due to too much phase separation. Through this method, a kind of macroporous material with adjustable macropore size can be obtained simply.

![Figure 1. SEM images of dried gels prepared with various W\(_{\text{PEO}}\): (A) 0.06 g of PEO, (B) 0.12 g of PEO, (C) 0.18 g of PEO, and (D) 0.24 g of PEO.](image)

Figure 2 shows the macropore size distribution of dried gels with different W\(_{\text{PEO}}\) using mercury porosimetry. It is easily observed that three xerogels have a narrow macropore size distribution, indicating macroscale phase separation that falls in the spinodal decomposition region. The macropore size of the three xerogels is distributed between 0.7 and 1.1 \(\mu\)m, enabling the application of the porous monolith for many purposes that require different pore sizes. The median macropore sizes of xerogels with W\(_{\text{PEO}}\) = 0.06, 0.12, and 0.18 g are 1.4, 1.1, and 0.85 \(\mu\)m, and the porosities are 75.35, 68.52, and 61.85% respectively, reflecting that the macropore size of the dried gels becomes smaller with the increase of W\(_{\text{PEO}}\). The results are well in accordance with the SEM morphology.

![Figure 2. Macropore sizes distribution of dried gels prepared with various W\(_{\text{PEO}}\) values: (a) 0.06 g of PEO, (b) 0.12 g of PEO, and (c) 0.18 g of PEO.](image)

Thermogravimetry–differential scanning calorimetry (TG–DSC) curves for gels are depicted in Figure 3. TG curve shows a total mass loss of 68.5 wt % from room-temperature to 1100
A large endothermic peak at around 100 °C and a weight loss as high as 20 wt % at 20–120 °C can be attributed to the evaporation of water and organic solvents, which also indicates that the resultant monolith has a high water-absorbing capacity. A little exothermic peak at 200 °C is related to the pyrolysis of organic species, such as residual PEO and halogenated alcohol, generated by the irreversible ring-opening reaction of protonated propylene oxide. The endothermic peak at 300 °C can be ascribed to the dehydroxylation of the calcium chloride precursor. A little exothermal peak near 400 °C is caused by decomposition of γ-AlOOH. The broad exothermic peak at around 500 °C is owing to the phase transformation from γ-AlOOH to γ-Al2O3 and decomposition of a little amount of residues. It can be observed that the transformation of nonequilibrium CaO and γ-Al2O3 to equilibrium C12A7 containing Cl takes place above 950 °C.

The as-dried sample with 0.12 g of PEO was chosen to carry out the heat-treatment and reduction in the subsequent steps.

Figure 4 depicts the appearance of the typical monolith (Figure 4A) and the morphologies of monoliths heat-treated at different temperatures. After heat-treatment, the appearance and structure of as-prepared porous monolith can be preserved perfectly with a little shrinkage, whereas the surface of the skeletons has become dense and smooth due to the removal of the residual organic matter during the process of the heat-treatment.

Similar to the dried gel sample, all of the samples heat-treated at different temperatures exhibit relative narrow macropore size distribution, which can be seen in Figure 5. The median macropore size and porosity of gels after being heat-treated at 700, 900, and 1100 °C are 0.7, 0.7, and 0.5 μm and 76.74, 76.97, and 78.67%, respectively. Compared with the dried
sample, the macropore size of the heat-treated samples decreases, whereas the porosity increases. The sample heat-treated at 1100 °C shows a porosity as high as 78.67%. The decrease of the pore size is caused by the shrinkage of the network, and the increase of porosity can be ascribed to the thermal decomposition of organic compositions in the skeletons. There is almost no mesopore in the skeleton of the C12A7 samples, which can be proved from the nitrogen adsorption–desorption isotherms of the mayenite samples (Figure S3).

XRD patterns of samples after being heat-treated at different temperatures are shown in Figure 6. No specific peaks are observed for the dried gel, indicating the amorphous structure. By comparing the XRD patterns with the standard data of Ca$_{12}$Al$_{14}$O$_{33}$ (C12A7) (PDF-09-0413 card) and Ca$_{12}$Al$_{14}$O$_{32}$Cl$_{2}$ (PDF-45-0568 card), it is seen that the XRD diffraction peaks of the samples heat-treated at different temperatures are in accordance with those of Ca$_{12}$Al$_{14}$O$_{32}$Cl$_{2}$ due to the utilization of the chloride precursors. A part of free oxygen ions in cages is replaced by the chlorine ions during heat-treatment, but the replacement has little influence on the reduction of the C12A7 due to much less electronegativity of the Cl$^-$ ions than that of the O$^{2-}$ ions. The result indicates that the C12A7 material has a cubic structure with a unit-cell content of Ca$_{24}$Al$_{28}$O$_{68}$ and the I43d space group. No other phases, such as CaAl$_2$O$_4$ (CA) or Ca$_3$Al$_6$O$_{14}$ (CSA3), are observed.

Figure 7 shows the transmission electron microscopy (TEM) image and scattering light spot of the sample after being heat-treated at 1100 °C. No specific peaks are observed for the dried gel, indicating the amorphous structure. By comparing the XRD patterns with the standard data of Ca$_{12}$Al$_{14}$O$_{33}$ (C12A7) (PDF-09-0413 card) and Ca$_{12}$Al$_{14}$O$_{32}$Cl$_{2}$ (PDF-45-0568 card), it is seen that the XRD diffraction peaks of the samples heat-treated at different temperatures are in accordance with those of Ca$_{12}$Al$_{14}$O$_{32}$Cl$_{2}$ due to the utilization of the chloride precursors. A part of free oxygen ions in cages is replaced by the chlorine ions during heat-treatment, but the replacement has little influence on the reduction of the C12A7 due to much less electronegativity of the Cl$^-$ ions than that of the O$^{2-}$ ions. The result indicates that the C12A7 material has a cubic structure with a unit-cell content of Ca$_{24}$Al$_{28}$O$_{68}$ and the I43d space group. No other phases, such as CaAl$_2$O$_4$ (CA) or Ca$_3$Al$_6$O$_{14}$ (CSA3), are observed.

Figure 8A exhibits the SEM image of the heat-treated sample after being further reduced at 900 °C. After reduction, the appearance and structure of the as-prepared porous mayenite monolith can still be largely preserved with the further shrinkage and collapse of skeletons of the macropores in some area. Although the structure of the reduction sample is a little broken compared to that of the as-dried and heat-treatment samples, the reduction has little influence on the continuous skeletons and interconnected macropores.

The macropore size distribution of the reduced sample is shown in Figure 8B. It is obviously seen that the sample, after reduction, has a relative wide macropore size distribution with a median pore size of about 0.6 μm. Although the macropore size distribution of the reduced samples is similar to that of the heat-treated samples, the porosity of the reduced sample slightly falls to 66.35%, resulting from the partial collapse of the C12A7 during the reduction.

Figure 9 shows the XRD patterns of the samples reduced at different temperatures. After reduction, whether there exists the Ca$_{12}$Al$_{14}$O$_{33}$ phase or not is uncertain judging from the XRD patterns due to the same peaks of Ca$_{12}$Al$_{14}$O$_{32}$Cl$_{2}$ and Ca$_{12}$Al$_{14}$O$_{33}$ except the intensity of the 211 peak. Obviously, compared with the heat-treated samples, there has been almost no change in peak positions after reduction but the 211 peak of the reduced samples is much higher than the one before reduction, which is closer to the C12A7 phase without chlorine elements. With the increase of the reduction temperature, the 211 peak rises obviously. It indicates that the cage structure has been reserved, the O$^{2-}$ ions as well as Cl$^-$ ions in the cage structure have been replaced by the e$^-$ successfully, and the reduction reaction and the replacement reaction have been carried out more thoroughly with the increase of the reduction temperature. The results confirm that the C12A7:e$^-$ forms and mayenite electride is obtained after reduction at high temperature.

The carrier concentration of macroporous mayenite electride after being reduced at different temperatures has been listed in Figure 10. The samples before reduction are absolutely insulating, which cannot be tested through the Hall effect. It is observed that the carrier concentration increases with the rise of the reduction temperature. A low carrier concentration of 1.119 $\times$ 10$^6$ cm$^{-3}$ is obtained at 500 °C, whereas a high reduction temperature of 1100 °C results in a high carrier concentration of 3.029 $\times$ 10$^{18}$ cm$^{-3}$. It confirms that the carrier concentration of the macroporous mayenite electride is closely related to the reduction temperature. Though, the Cl$^-$ ions are placed in a loose cage structure, the reduction reaction still needs a certain amount of energy to damage the covalent bond due to the strong electronegativity of the Cl$^-$ ions. A higher reduction temperature may promote the reduction reaction, which leads to a higher conversion percentage of the C12A7.

Figure 6. XRD patterns of the sample after being dried and heat-treated at different temperatures.
The carrier concentration can be reserved perfectly even after heat-treatment at 400 °C in air environment.

Figure 8. SEM image (A) and macropore size distribution (B) of the sample reduced at 900 °C.

Figure 9. XRD patterns of the samples reduced at different temperatures.

Figure 10. Carrier concentration of C12A7:e− reduced at different temperatures.

Figure 11 shows the TEM image of the sample and scattering light spot after being reduced at 900 °C. Compared with the heat-treated sample (Figure 7), it is clearly found that the multocrystals convert to complete the single crystal and the single crystal is C12A7:e− according to the XRD patterns (Figure 9). It further confirms that both Ca12Al14O32Cl2 and Ca12Al14O33 have been reduced to C12A7:e− after reduction.

Fourier transform infrared (FT-IR) spectra of the dried, heat-treated, and reduced samples are shown in Figure 12. It is found that the formamide (FA) and EG are distributed in the dried sample, whose main bands are as follows: stretching vibration of C−O groups (1692 cm−1), bending vibration of C−H bonds (880 cm−1), and stretching vibration of C−C bonds (1078 cm−1). After heat-treatment, all of the organic groups have been removed. The peaks at 572, 653, and 692 cm−1 are due to the Al−O stretching vibrations, and the peak at 1402 cm−1 is assigned to the Al−O vertical vibration. The peaks at about 300–400 cm−1 are attributed to the Ca2+ from the system. The peaks at 3417 and 1625 cm−1 correspond to the stretching vibrations and plane bending vibrations of O−H bending vibrations of water, respectively. There is almost no difference from spectra of heat-treated and reduced samples, which means that the component and structure of mayenite change a little after reduction. The weakness of bond strength of Al−O after reduction may be caused by the removal of the Cl− and O2− ions, which weakens the bond of the electrons around the “cages” and increases the electrons excited by the infrared ray. It also indicates that the reduction of the mayenite
has little influence of the cage structure, which results in that there is almost no chemical bond broken during reduction.

The Raman spectra of as-dried, heat-treated, and reduced samples are shown in Figure 13. It is seen that there are some Raman peaks in the as-dried sample, indicating numerous organic matters. These peaks can be removed after heat-treatment and reduction, and the main Raman peaks at 570, 770, and 1075 cm\(^{-1}\) occur, which are attributed to Al–O bond. The relative intensity of these three peaks is different, resulting from the change of the Al–O bond due to the removal of the O\(^2-\) ions or Cl\(^-\) ions.

Figure 14A shows the crystal structure of the C12A7. The cage space is occupied by the O\(^2-\) or Cl\(^-\) ions, and both ions have a strong electronegativity and easily form a covalent bond with other ions in the crystal. The process of the reduction is shown in Figure 14B; the reducing agent CaH\(_2\) could react with C12A7 through contact with C12A7 at high temperature and in vacuum environment. The loss of the O\(^2-\) and Cl\(^-\) ions releases the electrons bonded by the covalent bond and transforms to free electrons (shown in Figure 14C), which is similar to the n-type doped semiconductor.

Figure 14D shows the CASTEP DOS predictions for a single cell of C12A7 before and after reduction. From the DOS shown in Figure 14D, the Fermi level of C12A7 before reduction is just placed in the gap, which reveals that the C12A7 is an intrinsic semiconductor. Also, n-type conduction can be observed in C12A7 after reduction from Figure 14D, in which the Fermi level has just crossed the bottom of the conduction band. However, the DOS value near the Fermi level is not so high, declaring the limited conductive ability of the C12A7 after reduction. The calculated results are consistent with the results of the carrier concentration (Figure 10).

**CONCLUSIONS**

In summary, a kind of inorganic and room-temperature stable monolithic mayenite electride (C12A7:e\(^-\)) with co-continued skeletons and interconnected macropores has been successfully prepared via a sol–gel method accompanied by phase separation, followed by heat-treatment and a reduction process. An appropriate amount of PEO is utilized to form the macrostructure with adjustable macrosize and high porosity. The multicrys- tals Ca\(_{12}\)Al\(_{14}\)O\(_{32}\)Cl\(_2\) and Ca\(_{12}\)Al\(_{14}\)O\(_{33}\) (C12A7) precipitate after heat-treatment and transform to single-phase C12A7:e\(^-\) after reduction. The carrier concentration of mayenite electride (C12A7:e\(^-\)) increases with the reduction temperature and reaches 3.029 \(\times\) 10\(^{18}\) cm\(^{-3}\) when the reduction temperature rises to 1100 °C. Heat-treatment and reduction do not spoil the macrostructure of monolithic mayenite with high porosity. Such macroporous electron-encaged materials can be applied to different fields, such as electron emission, reducing agents, optoelectronic devices, oxygen-ion generation, and so on.

**EXPERIMENTAL SECTION**

**Materials.** Calcium chloride dihydrate (CaCl\(_2\)•2H\(_2\)O, Sigma-Aldrich Co., 99%) and aluminum chloride hexahydrate (AlCl\(_3\)•6H\(_2\)O, Sigma-Aldrich Co., 99%) were used as calcium source and aluminum source, respectively. A mixture of distilled water and ethanol (C\(_2\)H\(_6\)O: Sinopharm Chemical Reagent Co., Ltd, AR) was used as the solvent. Poly(ethylene oxide) (PEO: Aladdin Co., AR) with an average molecular weight (\(M_w\)) of 300 000 and propylene oxide (PO: Sigma-Aldrich Co., 99.5%) were added as the phase separation inducer and gelation agent, respectively. Glycol (EG: Sinopharm Chemical Reagent Co., Ltd, AR) and formamide (FA: Sinopharm Chemical Reagent Co., Ltd, AR) were utilized as the chelating agent and drying control chemical additive, respectively. CaH\(_2\) was used as a reductant to reduce the sample. All reagents were used as received without further purification.

**Synthesis.** The starting compositions are listed in Table 1. For a typical synthesis, first, 1.544 g of CaCl\(_2\)•2H\(_2\)O and 0.06–0.24 g of PEO were dissolved in H\(_2\)O/EtOH solution (1.80 mL of distilled water and 2.0 mL of EtOH were added, respectively). Then, 2.500 g of AlCl\(_3\)•6H\(_2\)O was added into the solution, 0.60 mL of EG and 0.70 mL of FA were added in sequence. After stirring at room-temperature for 2 h, the resultant homogeneous solution was cooled to zero in an ice/water bath and 2.0 mL of PO was added into the solution in a speed of 1 mL min\(^{-1}\). After stirring for 5 min, the obtained transparent solution was degassed by ultrasonication for about 20 s to remove the bubbles in the solution; thereafter it was...
gelated and aged at 45 °C for more than 24 h and then evaporated at 60 °C for more than 72 h. Some of the obtained xerogels were heat-treated at 700, 900, and 1100 °C for 2 h with a heating rate of 3 °C min⁻¹, respectively.

**Reduction.** The reduction of C12A7 monoliths heat-treated at 1100 °C was carried out in a dry crucible by 1.0 g of CaH₂ as reductant, sealed in an evacuated quartz glass tube under argon atmosphere protection (40 L min⁻¹). The reduction temperature and time were 500−1100 °C and 72 h, respectively. The reduced monolith was washed with EtOH. The color of the monolith changed from white to black after the reduction, and the monolithic shape was retained.

**Characterization.** The morphology and microstructure of the fractured surfaces of the dried gels and heat-treated gels were characterized by a scanning electron microscope (SEM, SU-70, Hitachi, Ltd., Japan). The macropore size distribution over the diameter from 20 nm to 100 mm of the dried gels and heat-treated gel monoliths were evaluated by mercury intrusion porosimetry (Belsorp mini II, Bel Japan Inc., Toyonaka, Japan, and AutoPore IV 9510, Micromeritics Instrument Corp.). The crystal structure of the samples after heat-treatment was confirmed by powder X-ray diffraction (XRD: Empyrean 200895, PAN analytical B.V., Holland). The porosity (%) of each sample was calculated as \[(1 - \rho_b/\rho_s) \times 100\], \(\rho_b\) and \(\rho_s\) are the bulk and skeletal densities, respectively. Carrier concentrations of C12A7:\(\text{e}^-\) were characterized by Hall measurement (HL5500, Nanometrics).

**Calculation.** The reduction process of C12A7 was calculated by the CAmbride Serial Total Energy Package (CASTEP) code. A model of C12A7 crystal structure was simulated by the program and the free oxygen ions were simulated to be replaced by the electrons. Thereafter, the density of state (DOS) of reduced C12A7 and the model of the crystal structure of reduced C12A7 had been calculated.

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**Table 1. Starting Compositions of the Samples in the Study**

| no. | AlCl₃·5H₂O/g | CaCl₂·2H₂O/g | FA/mL | EG/mL | PEO/g | H₂O/mL | EtOH/mL | PO/mL |
|-----|--------------|--------------|-------|-------|-------|---------|---------|-------|
| MP1 | 2.500        | 1.544        | 0.7   | 0.6   | 0.06  | 1.80    | 2.00    | 2.0   |
| MP2 | 2.500        | 1.544        | 0.7   | 0.6   | 0.12  | 1.80    | 2.00    | 2.0   |
| MP3 | 2.500        | 1.544        | 0.7   | 0.6   | 0.18  | 1.80    | 2.00    | 2.0   |
| MP4 | 2.500        | 1.544        | 0.7   | 0.6   | 0.24  | 1.80    | 2.00    | 2.0   |

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Figure 14. (A) Crystal structure of the C12A7, (B) schematic diagram of the reduction principle and (C) crystal structure of the C12A7:\(\text{e}^-\), and (D) density of states (DOS’s) of C12A7.

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**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01121.

Nitrogen adsorption−desorption isotherms of the mayenite samples, SEM image of the mayenite samples in different magnifications, and schematic diagram of the sol−gel process accompanied by phase separation of the Ca−Al−O system (PDF)
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