論文 / 著書情報
Article / Book Information

Title	Substitution of H ⁻ for O ⁻ and H ⁻ emissions of 12CaO·7Al ₂ O ₃
Authors	Fan Huang,Jiang Li,Hui Xian,Jing Tu,Jianqiu Sun,Shuqin Yu,Yoshifumi Torimot,Masayoshi Sadakata,Quanxin Li
Citation	Appl. Phys. Lett., Vol. 86, ,
Pub. date	2005, 3
URL	http://scitation.aip.org/content/aip/journal/apl
Copyright	Copyright (c) 2005 American Institute of Physics

Substitution of H^- for O^- and H^- emissions of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$

F. Huang, J. Li, H. Xian, J. Tu, J. Q. Sun, S. Q. Yu, and Q. X. Li^{a)}

Department of Chemical Physics, Lab of Clean Energy, University of Science & Technology of China, Hefei, Anhui, 230026, People's Republic of China

Y. Torimoto and M. Sadakata

Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

(Received 14 July 2004; accepted 3 February 2005; published online 7 March 2005)

By using an anion-exchanging method, about 90% of the O^- anions in the C12A7-O^- microporous crystal ($[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}\cdot 4\text{O}^-$) have been substituted primarily by the H^- anions, leading to the successful formation of a new H^- emission material, C12A7-H^- ($[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}\cdot 4\text{H}^-$). A sustainable and stable emission of H^- , in a current density of $\mu\text{A}/\text{cm}^2$ level, has been obtained by supplying H_2 and electrons on the backside of the C12A7-H^- sample. The emission features of C12A7-H^- , including temperature and field effects, have been investigated. It is expected that the present material could be practically used as an H^- anion generator. © 2005 American Institute of Physics. [DOI: 10.1063/1.1881785]

Anions have received considerable attention in recent years for their unique potential applications in chemistry and material field.^{1–8} For example, it has been found that anion implantation into insulated material surfaces is more suitable than using positive ion implantation due to negligible “surface charging-up” problem in the former.⁵ Anion is usually generated from a free electron attachment to an atom or a molecule in the presence of plasma, electron impact or other energetic irradiation.^{1,5,6} Since those processes are usually complicated and energetically costly with a low selectivity, developing a simpler approach to form a sustainable current and optional anion source is greatly needed. An attractive solution is to find a material that is able to store and emit our expected anions.

$12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7) is a microporous crystal, which has a positively charged lattice framework $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}$ per unit cell with a free space of 0.4 nm in diameter. The remaining two oxide ions O^{2-} (free oxygen) are trapped in the cages defined by the framework.^{9–13} The chemical formula for the unit cell may be represented as $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}\cdot 2\text{O}^{2-}$. Recently, it has been found that C12A7 can be transformed into C12A7-O^- ($[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}\cdot 4\text{O}^-$) under certain conditions.^{12,14} The O^- anions can be stored in the cages of C12A7-O^- and can also be emitted into the gas phase by applying an extraction field under suitable temperature.^{12,14,15}

In this contribution, we report that the H^- anions can substitute O^- anions in the C12A7-O^- microporous crystal, forming an emission material of H^- , C12A7-H^- ($[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}\cdot 4\text{H}^-$). A sustainable and stable H^- emission at a $\mu\text{A}/\text{cm}^2$ level current density was obtained by uptaking H_2 and electrons on the backside of the C12A7-H^- sample. It has been reported that H^- can be desorbed from metal hydride with a very weak H^- emission (about $10^{-4} \mu\text{A}/\text{cm}^2$),¹⁶ which is much lower than that of the C12A7-H^- sample. Therefore, we suggest that the

C12A7-H^- sample can be served as an efficient material for emitting H^- anions.

The preparation of the C12A7-O^- sample has been previously described:¹⁴ briefly, powders of CaCO_3 and $\gamma\text{-Al}_2\text{O}_3$ are mixed and grained at a molar ratio of $\text{CaCO}_3:\gamma\text{-Al}_2\text{O}_3=12:7$. The powder mixture is pressed to a pellet with a diameter of 15 mm and a thickness of 1.5 mm (if needed, the material size and shape can be varied). Then it is sintered at 1350°C for 18 h under flowing dry oxygen atmosphere. The C12A7-H^- sample was prepared by supplying H_2 gas (~ 2.0 Torr) and electrons (provided by a low negative dc voltage of -10 V) on the backside of the C12A7-O^- sample at 750°C for 10 h. Figure 1 is a schematic diagram for describing the substitution process. The H^- anions on the C12A7-O^- surface were generated by the surface electrochemical reaction: $\text{H}_2(\text{atmosphere}) + \text{e}^-(\text{surface}) \rightarrow \text{H}^-(\text{surface}) + \text{H}(\text{surface})$. Propelled by the external electric field (~ 67 V/cm) and thermal diffusion (750°C), H^- (surface) could enter the C12A7-O^- cages with O^- simultaneously desorbing from the C12A7-O^- crystals. We defined those H^- trapped samples as C12A7-H^- . The experimental apparatus for studying the material features is made up of three major parts: a sample chamber where the sample is mounted in the center of quartz tube; a picoammeter for measuring the total emission current; and a time of flight (TOF) mass spectrometer for measuring the relative intensity distribution among the anions emitted from the sample.

FIG. 1. A schematic description of the substitution processes of H^- for O^- in C12A7-O^- .

^{a)} Author to whom correspondence should be addressed; electronic mail: liqx@ustc.edu.cn

FIG. 2. TOF mass spectra for the C12A7- O^- sample with different treatment time (t): (a) $t=0$; (b) $t=30$ min; (c) $t=10$ h. Sample treatment condition: H_2 (2 Torr), voltage drop between two sides of the sample: -10 V, temperature: 750°C ; measurement condition: sample surface temperature: 750°C , ion extraction field: 500 V/cm.

The above substitution processes were demonstrated by the observation that an emission peak, H^- peak, appeared in the TOF spectra and increased with the density of O^- peak accordingly declining after uptaking H_2 and electrons on the backside of the C12A7- O^- sample. Experimentally, we measured the emitted species from the C12A7- O^- sample with different H_2 and electrons uptaking times (t) by TOF mass spectrometer. Figure 2(a) shows the emitted species from the C12A7- O^- sample without H_2 insertion ($t=0$). The major peak occurs at a mass number of 16, which corresponds to the O^- anions. There is also a small peak with a mass number near 0, which corresponds to electrons emitted from the sample surface. Figure 2(b) shows the emission spectrum for H_2 and electrons insertion time of 30 min. Here, other than the peaks of O^- and electron, a weak peak with a mass number of 1 corresponding to H^- appears. Figure 2(c) shows the emitted species after the sample has been treated for 10 h. The H^- peak becomes significantly stronger while the O^- peak becomes weak. The above results give an obvious evidence that the O^- anions in the C12A7- O^- have been substituted by the H^- anions. In Fig. 2(c), there is also a weak peak with the mass number of 17, which is attributed to the OH^- anions. The OH^- anions may be formed by the surface reaction between O^- (surface) and H (surface). Furthermore, the x-ray diffraction results show that there is no obvious changes before and after H^- substitution process, which means that exchanging the encaged O^- by H^- would not influence the sample's crystal structure.

The emission ratio does not always directly represent the substitution ratio due to their different rates of diffusion and desorption for H^- and O^- , which mainly depend on temperature. Therefore, we measured the emission intensities of the anions as a function of the sample temperature. It was found that the emission intensity of H^- remarkably increased when the sample temperature increased from 650 to 800°C . There was only H^- emission observed at 650°C , and with temperature rising, the emissions of O^- and OH^- appeared and the emission intensity ratios $I(H^-):I(O^-):I(OH^-)$ slightly decreased and reached ratios of $0.8:0.1:0.1$ at 750°C . With sample temperature higher than 750°C , the emission intensity ratio was nearly independent of temperature. These results indicate that the emission ratio could be farthest near the substitution ratio in the high temperature region. Accordingly, we consider that about 90% O^- in C12A7- O^- has been substituted by H^- (80%) and OH^- (10%) by using the anion-

FIG. 3. H^- emission current densities measured as the functions of: (a) sample temperature at 500 V/cm and (b) ion extraction field at 800°C .

exchanging method, which leads to the formation of the H^- emission material C12A7- H^- .

The absolute emission current densities of H^- can be derived from the relative intensity distribution of the emitted species detected by the TOF spectra and the total emission current simultaneously measured by a picoammeter. Figure 3(a) gives the H^- emission current densities as a function of the sample temperature in an ion extraction field of 500 V/cm. When temperature rises from 600 to 803°C , the emission current density increases more than three orders of magnitude. Another factor that influences the current densities is the ion extraction field. Figure 3(b) shows a typical relation between the H^- emission current density and the ion extraction field at a given temperature of 800°C . As the ion extraction field increases, H^- emission current density increases significantly. The maximum H^- emission current density reaches $2.3 \mu\text{A}/\text{cm}^2$ under our investigated ranges. Due to the certain amount of anions in the sample cages, the emission current gradually decreases with increasing the emission time. It was found that under sample temperature of 800°C and an ion extraction field of 980 V/cm, the H^- current dropped to half with 10 h emission. However, this drop can be recovered by supplying H_2 (~ 2.0 Torr) and electrons (provided by a low negative dc voltage of -10 V) on the backside of the sample for 2 h at 750°C . Furthermore, a sustainable and stable emission current can be achieved by continuously supplying H_2 and electrons on the backside of the C12A7- H^- sample. Figure 4 shows the stability of the H^- emission current density at a given temperature of 800°C and ion extraction field of 980 V/cm. Along with continuously increasing emission time, we could detect only small fluctuations without obvious decrease, which means that C12A7- H^- sample can be practically used to generate sustainable and stable H^- emission.

FIG. 4. H^- emission current density vs emission time at C12A7- H^- sample temperature of 800°C and an ion extraction field of 980 V/cm.

Two basic types of H^- ion sources have been well developed, where either the H^- anions are formed in the H_2 plasma by dissociate attachment process (referred to as “volume source”) or by sputtering technology when an H^+ ion strikes a negatively biased surface coated with the cesium/barium film (referred to as “surface source”).^{17,18} In comparison with the previous methods, the advantages of the present H^- source would be its simplicity, high selectivity for producing special anions, long permanence, and the fact that it can be operated either in high vacuum or 1 atm. However, the current density of H^- we obtained is still quite lower than that in plasma or sputtering method. We expect that the H^- current density can be further increased by increasing the extraction field, surface temperature, modifying the emission material composition and changing the material shape, and using ion-focusing and high-voltage acceleration.

In conclusion, we have reported a high degree substitution of H^- for O^- in the C12A7-O^- microporous crystal by the anion-exchanging method. About 90% of the O^- anions in the cages of C12A7-O^- have been substituted mostly by H^- anions and a few OH^- anions, forming an H^- -emission material (C12A7-H^-). We suggest that this anion-exchanging method can be extended to other mono-charge anions such as OH^- , Cl^- , etc. The emission characteristics of C12A7-H^- , including the temperature and field effects as well as the emission stability of H^- , have been investigated. The C12A7-H^- sample prepared by this method can emit a $\mu\text{A}/\text{cm}^2$ level H^- current to the gas phase. It can be expected that the H^- current density can be further increased by increasing the extraction field, surface temperature, modifying the emission material composition, and using ion-focusing and high-voltage acceleration.

The authors thank T. Dong and L. Wang for the material synthesis. Q.X.L. thanks the support of the “BRP program” by the Chinese Academy of Sciences.

- ¹J. Lee and J. J. Grabowski, Chem. Rev. (Washington, D.C.) **92**, 1611 (1992).
- ²T. Tashiro, T. Watanabe, M. Kawasaki, and K. Toi, J. Chem. Soc., Faraday Trans. **89**, 1263 (1993).
- ³S. G. Neophytides, D. Tsiplakides, P. Stonehart, M. M. Jaksic, and C. G. Vayenas, Nature (London) **370**, 45 (1994).
- ⁴J. S. Valentine, *Active Oxygen in Biochemistry* (Blackie, London, 1995).
- ⁵J. Ishikawa, Rev. Sci. Instrum. **67**, 1410 (1996).
- ⁶M. Born, S. Ingemann, and N. M. M. Nibbering, Mass Spectrom. Rev. **16**, 181 (1997).
- ⁷D. V. Deubel and G. Frenking, J. Am. Chem. Soc. **121**, 2021 (1999).
- ⁸R. W. Fessenden, D. Meisel, and D. M. Camaioni, J. Am. Chem. Soc. **122**, 3773 (2000).
- ⁹J. Jeevaratnam, F. P. Glasser, and L. S. D. Glasser, J. Am. Ceram. Soc. **47**, 105 (1964).
- ¹⁰J. A. Imlach, L. S. D. Glasser, and F. P. Glasser, Cem. Concr. Res. **1**, 57 (1971).
- ¹¹H. Hosono and Y. Abe, Inorg. Chem. **26**, 1192 (1987).
- ¹²K. Hayashi, M. Hirano, S. Matsuishi, and H. Hosono, J. Am. Chem. Soc. **124**, 738 (2002).
- ¹³S. Watauchi, I. Tanaka, K. Hayashi, M. Hirano, and H. Hosono, J. Cryst. Growth **237**, 496 (2002).
- ¹⁴Q. X. Li, K. Hayashi, M. Nishioka, H. Kashiwagi, M. Hirano, H. Hosono, and M. Sadakata, Appl. Phys. Lett. **80**, 4259 (2002).
- ¹⁵Q. X. Li, H. Hosono, M. Hirano, K. Hayashi, M. Nishioka, H. Kashiwagi, Y. Torimoto, and M. Sadakata, Surf. Sci. **527**, 100 (2003).
- ¹⁶H. Kawano, A. Tanaka, S. Sugimoto, T. Iseki, Y. Zhu, M. Wada, and M. Sasao, Rev. Sci. Instrum. **71**, 853 (2000).
- ¹⁷A. J. T. Holmes, Plasma Phys. Controlled Fusion **34**, 653 (1992).
- ¹⁸W. C. Wang, Y. Xu, W. G. Wang, and A. M. Zhu, J. Phys. D **37**, 1185 (2004).