Erosion Mechanism of Li-Ion Batteries Cathode Materials on Si$_3$N$_4$-SiC and SiO$_2$-SiC Refractories

X K Duan$^1$, F Qian$^1$, Y Q Chen$^{1,2}$, H X Li$^{1,2}$, A Guo$^1$, Y C Si$^1$, X F Wang$^1$*, G Q Liu$^1$*

$^1$ State Key Laboratory of Advanced Refractories, Sinosteel Luoyang Institute of Refractories Research Co., Ltd., Luoyang 471039, Henan, China
$^2$ School of Materials Science and Engineering, Zhengzhou University, Henan 450001, China

Corresponding author’s e-mail address: G Q Liu: liugq@lirrc.com

Abstract. The erosion mechanism of Li-ion ternary cathode material on Si$_3$N$_4$-SiC and SiO$_2$-SiC refractory slabs was studied at 780 °C for 20h. The results show that the erosion resistance of Si$_3$N$_4$-SiC is much better than that of SiO$_2$-SiC refractory slab after heat treatment for 20h. Erosion mechanism of the two kinds of refractory slabs are different. Inward diffusion of Li$_2$O reacts with a large amount of SiO$_2$ in the SiO$_2$-SiC system. This leads to a large number of reaction products, so that the incompletely reacted SiC particles fall off along with the reaction product, causing the erosion of SiO$_2$-SiC. For Si$_3$N$_4$-SiC, it is mainly because the dense SiO$_2$ protective layer produced by oxidation of Si$_3$N$_4$ prevents further oxidation of Si$_3$N$_4$ and SiC in the system, giving the material excellent erosion resistance.

1. Introduction

Lithium-ion batteries with high volumetric and gravimetry energy density are widely used in mobile communications, military, information science fields and new energy vehicles [1,2,3]. As a core material for Li-ion batteries, the main commercial cathode materials are LiMn$_2$O$_4$, LiCoO$_2$, LiMPO$_4$ (M=Fe, Mn) and ternary cathode materials. Among which ternary cathode materials have highest energy density, especially the Ni-rich ternary cathode materials (Ni content > 0.6), which have attracted wide attention in the Li-ion battery industry [4,5,6]. Most of the cathode materials are carried on refractory saggars, then put in refractory kiln using high temperature solid-phase synthesis methods. The equipment and production process are simple, and it is one of the most commonly used synthetic methods in industrial production [7,8]. Currently, with the raw materials are cheap, the good high temperature mechanical properties and low coefficient of thermal expansion [9], the saggar materials used is mostly cordierite-mullite composite materials. As cathode materials for lithium-ion batteries develop, the lithium source of the rapidly developing Ni-rich ternary cathode materials is more aggressive than that of other conventional cathode materials, including LiMn$_2$O$_4$, LiCoO$_2$, LiMPO$_4$ (M=Fe, Mn) and common ternary cathode materials [10,11]. As the nickel content increases, the time for synthesizing the Ni-rich ternary cathode material is longer than that of the common cathode material, and the erosion time of the saggar is longer, which makes saggar more vulnerable to damage. At present, the saggars used can be used approximately 10-15 times, but generally they start to appear slightly peeling slag around 4 times, and gradually aggravate. This will contaminate the cathode materials, affect the quality and performance of the cathode materials and wasting resources. SiC-
based refractory like Si$_3$N$_4$-SiC and SiO$_2$-SiC refractory have excellent properties such as high temperature strength, strong oxidation resistance, good wear resistance, and resistance to chemical erosion [12,13,14,15]. It has been widely used in various fields, but there are less studies on the synthesis of cathode materials, and fewer research on its erosion mechanism. In our present work, we select Si$_3$N$_4$-SiC and SiO$_2$-SiC as the refractory slab materials. After mixing Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (LNCM811) precursor with LiOH·H$_2$O, they are placed on the selected refractory slabs for heat treatment. Since the erosion of the refractory materials is mainly caused by LiOH·H$_2$O, and at the same time, the reactants between LNCM materials and refractory slab each time is little, so the amount of LiOH·H$_2$O was appropriately increased and adjusted in this experiment [16,17]. The interactions between Si$_3$N$_4$-SiC and SiO$_2$-SiC as the refractory slabs during the synthesis of ternary cathode materials are studied. The oxidation resistance and erosion mechanism of the two materials was also investigated.

2. Materials and methods

2.1. Materials preparation

The precursor LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (LNCM811) mixture powders was obtained as follows. Purchased Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$(OH)$_2$ precursor is mixed with LiOH·H$_2$O in a weight ratio of 40:60. After thorough mixing, the mixed powders were weighed to 10 g and placed on Si$_3$N$_4$-SiC and SiO$_2$-SiC refractory slabs fixed to the tile diameter (Apparent porosity: 12.0%, 24.0%, respectively, supplied by Sinosteel Luoyang Institute of Refractories Research Co., Ltd, Luoyang, China). Two kinds of refractory slabs both have a thickness of about 1cm. Next, the refractory slabs with the mixed powders were heat-treated in an electric furnace at 780°C for 20 hours. Then, observe the surface and longitudinal section of the refractory slab after the reaction, and measure the thickness of the reaction layer. Meanwhile, select a 3 mm thick refractory slabs containing the reaction layer for X-ray diffraction to find the phase composition. The refractory slabs after heat-treated were impregnated in low-viscosity resin, polished for further scanning electron microscopy (SEM). As for the erosion mechanism experiment, the LiNCM811 mixed powders and the SiC powder are uniformly mixed in a weight ratio of 1:1. Next, the uniformly mixed powders are heat-treated at 780°C for 20 hours. The treated powders were ground and analysed for further X-ray diffraction (XRD).

Figure 1. The appearance of Si$_3$N$_4$-SiC refractory slab sample after heat treatment at 780°C for 20h (a) the appearance top view (b) top view after LNCM materials removed (c) Longitudinal section.
2.2. Sample characterization techniques
The X-ray diffraction (XRD,) is used to determine the phase composition of the reaction where as scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) to investigate the morphological changes occurring after heat treatment

3. Results and discussion

3.1. Appearance of the sample after heat treatment
Figure 1 and Figure 2 show the appearance of the two kinds of samples after heat treatment, respectively. In Figure 1a and Figure 2a, the LNCM811 mixed powders show signs of melting after heat treatment, and both samples were subjected to different degrees of erosion after heat treatment. From the results, the thickness of the reaction slag layer of Si₃N₄-SiC is 1.5mm (Figure 1c), while that of SiO₂-SiC is 2.5mm (Figure 2c). This indicates that the reaction of LNCM811 materials and SiO₂-SiC is more severe than the reaction of LNCM811 materials and Si₃N₄-SiC (Figure1b and Figure2b).

3.2. Characterization analysis

3.2.1. XRD analysis of the sample. The phase composition of Si₃N₄-SiC after firing for 20 h is shown in Figure 3. During the sintering process, Si₃N₄-SiC reacts with battery materials powder to produce various products. SiC is the main phase, along with Li₂SiO₃ (lithium metasilicate), Li₅SiO₄ (lithium orthosilicate), Si₃N₄ (silicon nitride) and Li₀.₄Ni₁.₆O₂ (lithium Nickel oxide). Among them, SiC and Si₃N₄ come from unreacted refractory slab, however, the lithium-containing substances in Figure 3 such as Li₂SiO₃ (lithium orthosilicate), Li₅SiO₄ (lithium orthosilicate) and Li₀.₄Ni₁.₆O₂ (lithium Nickel oxide) is produced during the reaction between the battery materials and the refractory slab. Li₀.₄Ni₁.₆O₂ is the product of cathode materials for synthetic battery. The observed Li₂SiO₃, Li₅SiO₄ and SiO₂ should be generated from the following reaction. May be due to low content, as the intermediate product Si₂N₂O of Si₃N₄ oxidation is not detected. The results of XRD indicate that Si₃N₄ is preferentially oxidized to SiC, which is consistent with what has been reported in the literature [18].
Figure 3. XRD patterns of Si$_3$N$_4$-SiC refractory slab treated at 780°C for 20h.

Figure 4. XRD patterns of SiO$_2$-SiC refractory slab treated at 780°C for 20h.

\[ 4\text{Si}_3\text{N}_4 + 3\text{O}_2 = 6\text{Si}_2\text{N}_2\text{O} + 2\text{N}_2 \]  
(1)

\[ 2\text{Si}_3\text{N}_2\text{O} + 3\text{O}_2 = 4\text{SiO}_2 + 2\text{N}_2 \]  
(2)

\[ \text{SiO}_2 + \text{Li}_2\text{O} = \text{Li}_2\text{SiO}_3 \]  
(3)

\[ \text{Li}_2\text{SiO}_3 + \text{Li}_2\text{O} = \text{Li}_4\text{SiO}_4 \]  
(4)

Figure 4 shows the phase composition of SiO$_2$-SiC after reaction. It can be seen that, the main phase after reaction is still SiC, and Li$_2$SiO$_3$ and Li$_4$SiO$_4$ are also present. By comparing Figure 3 and Figure 4, it is shown that the content of Li$_4$SiO$_4$ has decreased, and the main product is Li$_2$SiO$_3$. This
probably because the SiO₂ content in SiO₂-SiC is higher than Si₃N₄-SiC, and the inwardly permeable Li₂O is easier to react with SiO₂ to form Li₂SiO₃. In Si₃N₄-SiC refractory slab, SiO₂ is produced by oxidation of Si₃N₄, and the content is less, so the generated Li₂SiO₃ further reacts with Li₂O to produce Li₄SiO₄ [19].

3.2.2. SEM analysis. The microstructure of Si₃N₄-SiC after heat treatment is presented in Figure 5. The upper layer in the figure is the inner surface of the slab contacting the battery material, and the lower layer is the outer surface. The outer surface (Figure 5b) shows the original morphology of Si₃N₄-SiC. As can be seen, the matrix of the saggar is porous Si₃N₄, adding large SiC particles. Figure 5a is clearly divided into three layers except the original layer. The first layer is the outermost dark-gray material (marked as 3 in Figure 5d), the second layer is the gray (noted as 2 in Figure 5c) and the third layer is the light-gray matter around the particles (labeled as 1 in Figure 5c). The deeper the color, the greater the degree of oxidation, all oxidation products should contain element Li as well. Combined with the EDS and XRD results, the outermost dark-gray material should be Li₄SiO₄, and the gray and light-gray matter are intermediates of the reaction between the Li₂O and SiO₂. For Si₃N₄-SiC, the erosion is mainly caused by the inwardly diffusing Li₂O, and preferentially erodes the matrix, and then reacts with the SiC particles. In Figure 5c and 5d, cracks can be observed between the newly formed phases and particles, which may lead to exfoliation of the sample.

The results of SEM of SiO₂-SiC after etched by LNCM are shown in Figure 6. Left to right in figure is the order of refractory slab from inner surface to outer surface. It can be clearly seen that different products are generated by the reaction, on the far left in the figure shows the residual SiC particles and the black reaction product to be peeled off (Figure 6a). At the same time, there are many transverse cracks in the dark-gray material parallel to the slab. These cracks may cause the unreacted
SiC particles to fall off, which seriously affects the corrosion resistance of the material. The macroscopic appearance in Figure 1c and Figure 2c above is also consistent with this. A higher multiple SEM image is presented in Figure 6b. The results of EDS in Figure 6b show that the oxidation degree of different colour areas is different, which is the same as that of Si$_3$N$_4$-SiC. The darker the colour, the higher the oxygen content, and it is speculated that it is the same substance as that of Si$_3$N$_4$-SiC. The dark-gray material should be Li$_4$SiO$_4$, and the gray and light-gray matter are intermediates of the reaction between the Li$_2$O and SiO$_2$.

![Figure 6. BSE images of SiO$_2$-SiC refractory slab after heat treatment](image)

Figure 6. BSE images of SiO$_2$-SiC refractory slab after heat treatment (a) inner surface (b) higher magnification of the inner surface P: pore; Cra: crack

![Figure 7. XRD patterns of LNCM materials and SiC mixed powders after reaction at 780°C for 20h.](image)

Figure 7. XRD patterns of LNCM materials and SiC mixed powders after reaction at 780°C for 20h.

3.2.3. Analysis of erosion mechanism. In order to explore the erosion resistance of SiC-based refractories, a study was carried out in the experimental range: The SiC powder and the battery materials were uniformly mixed for heat treatment. The results of XRD and SEM were as follows. Figure 7 shows the XRD spectrum after the reaction. Comparing Figure 3, Figure 4 and Figure 7, it can be seen from the figures that when SiC reacts with the battery materials powder, the different treatment methods are different. By way of comparison the reaction refractory slab, the heat treatment after mixing the sample directly, SiC most complete reaction. It is worth mentioning that the main reaction product is the further product Li$_2$SiO$_3$, Li$_4$SiO$_4$, when the reaction mode is carried out through
the refractory slab, while, after the direct reaction after mixing, the main phase composition is the primary reaction product Li₂Si₂O₅. When the reaction mode is a refractory slab, Li₂O is more difficult to penetrate than the loose powdered SiC because of the compact arrangement of the substances in the refractory slab. In the case of powdery SiC, the infiltration of Li₂O inward is faster, reacts faster, and tends to be more inclined to reaction generated primary product primary products Li₂Si₂O₅ in the reaction due to the reduced resistance.

The SEM results are presented in Figure 8. After heat treatment, the bright white battery materials aggregates were uniformly distributed in the sample with gray Li₂Si₂O₅ and light gray SiC particles. Since the SiC particles are small, and the direct heat treatment after powder mixing, so the reaction resistance is small, and a plurality of gray floc Li₂Si₂O₅ can be seen in the field of view to surround the unreacted light gray SiC particles (Figure 8a). A high-magnification SEM image is shown in Figure 8b. The area 1 is gray Li₂Si₂O₅. Comparing with the energy spectrum results of the refractory slab (Figure 5 and Figure 6), it can be found that in addition to the original elements in the refractory slab, the Ni element in the battery materials appears. This may be due to the fact that when the reaction mode is a refractory slab, in addition to the inward diffusion of Li₂O, other elements of Ni, Co, and Mn of the battery materials also diffuse inward, but since the rate of diffusion of these substances is much smaller than that of Li₂O, they are peeled off together with unreacted SiC particles and reactants when they have not penetrated into the inside of the refractory slab. When the powder is directly mixed and reacted, the oxygen is diffused inward more easily. Further, under the induction of oxygen, SiC reacts with O₂ to form a dense SiO₂ layer to prevent further internal oxidation. The generated SiO₂ reacts with the inward diffused Li₂O to produce silicate compound, causing material erosion [18,20].

![Figure 8. BSE images of LNCM materials and SiC mixed powers (a) low magnification (b) high magnification.](image)

4. Conclusions
The erosion reaction was explored in the synthesis process of actual ternary cathode materials of Li-ion batteries on SiO₂-SiC and Si₃N₄-SiC refractory slabs. The two materials show different erosion resistance, and Si₃N₄-SiC has better erosion resistance than SiO₂-SiC refractory slab. For SiO₂-SiC, a large amount of SiO₂ in the system makes the inward diffusion of Li₂O easier to react with, so a large amount of Li₂SiO₃ product is produced, and Li₂SiO₄ is less. In terms of Si₃N₄-SiC, this mainly was attributed to the oxidation of Si₃N₄ in Si₃N₄-SiC refractory slabs to produce dense SiO₂ protective layer, which then reacts with Li₂O that penetrates inward to form Li-containing substances such as Li₂SiO₃, Li₄SiO₆. Meanwhile, the resulting dense SiO₂ protective layer can further prevent the oxidation of Si₃N₄ and SiC, so that the material obtains better erosion resistance.

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References

[1] Li L J, Li X H, Wang Z X, Guo H J, Peng Y, Wei C and Ling W 2011 Powder Technol. 206 353
[2] Liang H M, Wang Z X, Guo H J, Wang J X and Leng J 2017 Appl. Surf. Sci. 423 1045
[3] Xiao Z L, Hu C M, Song L B, Li L J, Cao Z, Zhu H L, Liu J, Li X Y and Tang, F L 2017 Ionics 24 1
[4] Liu W, Oh P, Liu X, Lee M-J, Cho W, Chae S J, Kim Y and Cho, J 2015 Angew. Chem. Int. Ed. 54 4440
[5] Vu D L and Lee J W 2015 Korean J. Chem. Eng. 33 514
[6] Huang Y, Wang Z X, Li X H, Guo H J and Wang J X 2015 Trans. Nonferrous Met. Soc. China 25 2253
[7] Ju S H and Kang Y C 2008 J. Power Sources 178 387
[8] Zhang Z L, Chen D H and Chang C K 2017 RSC Adv. 7 51721
[9] Albhilil A A, Kozánková J and Palou M 2013 J. Sci. Eng. 39 67
[10] Kostecki R and McLarnon F 2004 Electrochem. Solid-State Lett. 7 A380
[11] Hu G R, Liu W M, Peng Z D, Du K and Cao Y B 2012 J. Power Sources 198 258
[12] Lange F F 1973 J. Am. Ceram. Soc. 56 445
[13] Park H, Kim H W and Kim H E 2005 J. Am. Ceram. Soc. 81 2130
[14] Guan L, Fan B B, Li M L, Wen H J, Li K, Wang H L, Chen D and Zhang R 2010 Key Eng. Mater. 434 435
[15] Suzuki A, Ashida H, Furui N, Mameno K and Matsunami H 1982 Jpn. J. Appl. Phys. 21 579
[16] Zhai P T, Chen L G, Yin Y M, Li S P, Ding D F and Ye G Y 2018 J. Eur. Ceram. Soc. 38 2145
[17] Zhai P T, Chen L G, Hu S H, Zhang X, Ding D F, Li H X, Li S P, Zhu L L and Ye G T 2018 Int. J. Appl. Ceram. Technol. 16 287
[18] Zhai Y W, Li Y, Liu L, Zhu X Y, Wang J P and Sun J L 2011 Adv. Mater. Res. 194-196 1564
[19] Eppler R A 1963 J. Am. Ceram. Soc. 46 97
[20] Yang X M, et al. 2016 Corros. Sci. 103 165