INVESTIGATION ON THE INTERACTIONS BETWEEN CORDIERITE AND LI-ION BATTERY CATHODE MATERIALS DURING CALCINATIONS

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ABSTRACT

To identify the interactions between Li-ion battery cathode materials and the cordierite containing saggar matrix during the industrial calcinations, mixtures of cordierite powder (0.074mm) and commercial Li-ion battery cathode materials were fired at different temperatures between 800 °C and 1000 °C. The phase development in the interactions between cordierite and Li-ion battery cathode materials during heat treatment was investigated by X-ray power diffraction (XRD). The reaction interface and diffusion coefficient were observed by scanning electron microscopy (SEM). Additionally, the reaction extents at different temperatures were confirmed by the sample diameter change analysis. Based on these experimental results, the corrosion mechanism of cordierite saggar matrix by Li-ion battery cathode materials is discussed.

INTRODUCTION

Ternary Li-ion battery cathode $Li(Ni_xCo_yMn_z)O_2$ (LNCM) materials are used as the efficient energy storage strategy for a wide range of portable devices, like cellular phones, laptops and digital electronics, and hybrid electric vehicles and pure electric vehicles, due to their high specific capacity, low cost, long cyclic life, and both structural and thermal stability[1,2]. Various approaches, such as co-precipitation, sol-gel, solid state reaction, hydrothermal, micro-emulsion, and pyrolysis methods[3-5], have been employed to prepare high-quality LNCM materials because the crystals size, phase composition, particle morphology and surface area of the materials, are strongly dependent on the synthesis route and can affect the performance of the battery[3]. However, the synthesis method only based on solid-state reaction has been industrially employed to prepare LNCM materials with a large quantity. In such preparation process, the calcination temperatures are normally at about 1000 ºC to favor the crystal growth of LNCM, thereby obtaining LNCM materials with appropriate crystals[7].

Cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) was commonly employed to enhance the thermal shock resistance of refractory saggars and is used in the saggars to prepare LNCM materials based on solid state reaction，due its low thermal expansion coefficient. A challenge of the application of saggars is that serious corrosion and spalling of the saggers contacting with LNCM cathode materials can inevitably occur during the calcination, especially when the heat-treatment temperature reaches 1000 ºC to attain appropriate LNCM crystals distribution. Therefore, the knowledge of the interfacial reactions between cordierite and LNCM materials during calcination is indispensable in controlling and improving both the overall life-time of the saggers and the cleanliness of the LNCM cathode materials.

Nevertheless, there are no experimental results providing insights in the degradation mechanism of cordierite containing saggar materials in contact with LNCM materials. The object of this study is to investigate the degradation behavior of cordierite materials in contact with LNCM during calcinations, using an experimental approach which has been used to evaluate the refractory materials alkali corrosion resistance[7,8].

EXPERIMENTAL

$Li(Ni_xCo_yMn_z)O_2$ (LNCM) precursor was prepared by mixing commercially available Li_2CO_3 (≥99.0 wt% purity) and $Ni_{0.5}Co_{0.2}Mn_{0.3}(OH)_2$ (≥99.0 wt% purity) powders in a weight ratio of 30:70. The LNCM precursor powders were dry-mixed with cordierite grains (below 0.074mm) in a weight ratio of 30:70, added with 3 wt% of yellow dextrin as the plasticizer, for 100 min in a rotary mill using zirconia balls as mixing medias. Then, 3 wt% of water was added for 10 min wet-mixing and the balls/powder weight ratio is 1:1. After mixing, the mixture was compacted to cylinders (36mm in diameter and about 8mm in height) at 50 MPa with a uniaxial press. The obtained cylinders were dried at 110 °C for 24 h, and calcined at different temperatures ranging from 800 ºC to 1000 ºC for 6 h.

The diameters of cylinders before and after calcinations were measured to assess the expansion caused by the interfacial reactions. Phase compositions were examined with X-ray powder diffraction (XRD) to examine the extents of interfacial reactions between cordierite and LNCM materials. Microstructure at cordierite grain/LNCM interface of the samples after calcinations was observed by scanning electron microscopy (SEM) at 15kV and 3kV.

RESULTS AND DISCUSSION

It is seen in Fig. 1 that diameters of the mixture samples are all expanded after calcinations at 800 ºC, 900 ºC, 1000 ºC and 1100 ºC respectively. This expansion should be ascribed to the low density reaction products formed during calcination. As indicated in Fig. 1, the rate of expansion for the sample after heat treatment at 800 ºC is 1.24% and that of the sample after heat treatment at 900 ºC to 1.52%, indicating that there is only a minor increase of 0.28% when the temperature was increased from 800 ºC to 900 ºC.

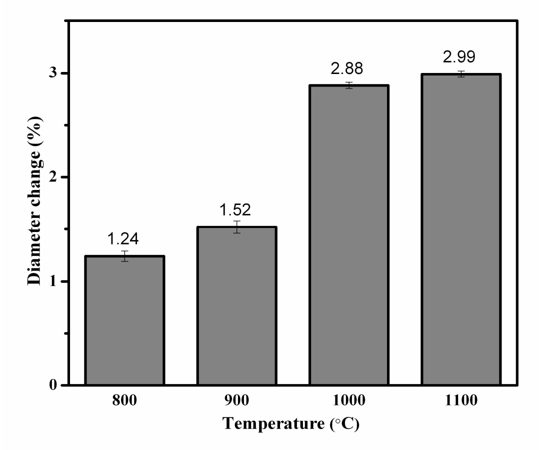

Fig. 1: Diameter change of samples after heat treatment at different temperatures.

However, the rate of expansion for the sample after heat treatment at 1000 ºC 2.88%, indicating that there is a large increase in the amount of 1.36% when the temperature was increased from 900 ºC to 1000 ºC. Meanwhile, the expansion rate of the sample after heat treatment at 1100 ºC was 2.99%, meaning that the expansion rate increases by 0.11% when the temperature was increased from 1000 ºC to 1100 ºC. It could be inferred that different expansion rates of the mixture samples may be dependent by the extents of reactions at the heat treatment temperature. In other words, the expansion rate of the samples are greatly increased from 900 ºC to 1000 ºC because that the reaction extent has been noticeably promoted when the temperature was increased in this region.

It is seen in Fig. 2 that $LiAlSiO_4$ (eucryptite) was formed in the samples after calcinations in the temperature range between 800 ºC and 1100 ºC. However, the peaks of $LiAlSiO_4$ are not much increase when the temperature was increased from 800 ºC to 900 ºC, indicating that the reactions between cordierite and LNCM does not increase much in this temperature range. In contrast, the amount of $LiAlSiO_4$ shows a large increase when the temperature changes from 900 ºC to 1000 ºC, indicating that the reactions between cordierite and LNCM have increased noticeably in this temperature range. This should be the reason why a massive expansion of samples diameters occurred after calcination when the temperature increases from 900 ºC to 1000ºC (see Fig. 1).

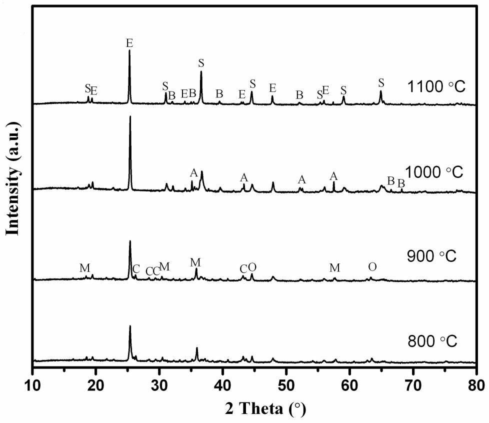

Fig. 2: X-ray diffraction patterns of the samples after heat treatment at different temperatures (S: spinel ($MgAl_2O_4$), powder diffraction file No. 01-075-1800; E: eucryptite ($LiAlSiO_4$), powder diffraction file No. 00-026-0480; M: manganese cobalt oxide ($MnCo_2O_4$), powder diffraction file No. 01-084-0482; B: cobalt silicate (Co_2SiO_4), powder diffraction file No. 01-076-1501; C: cordierite ($Mg_2Al_4Si_5O_{18}$), powder diffraction file No. 00-013-0294; O: olivine $(Co_{0.5}Mg_{0.5})_2SiO_4$ powder diffraction file No. 00-087-0057; A: corundum (Al_2O_3) powder diffraction file No. 01-074-1081).

However, the peaks of $LiAlSiO_4$ are a little lower at the temperature of 1100 ºC compare with 1000 ºC. Meanwhile, the amount of $MgAl_2O_4$ (spinel) at the temperature of 1100 ºC is higher than that at 1000 ºC. It is also interesting to note in Fig. 2 that a small amount of Al_2O_3 (corundum) only appears at 1000 ºC, indicating that the Al_2O_3 began to precipitate from Li_2O-Al_2O_3-SiO_2 ternary system and reacted with MgO from cordierite to form $MgAl_2O_4$ when the temperature is above 1000ºC.

Various reaction products were formed during calcinations at different temperatures. In generally, the different extent of chemical reactions occurred and reaction products were formed between cordierite and LNCM cathode materials during calcinations. The chemical reaction was sharply accelerated when the temperature increase from 900 ºC to 1000 ºC, accompanied by these chemical reactions the amount and types of the products changed constantly. The large amount of low density $LiAlSiO_4$ formation may promote the expansion of the samples, and lead to a local stress and the degradation of cordierite containing saggar materials.

In the process of LNCM materials calcination, the cordierite-containing saggars were used in recycle of calcinations and cooling down, much more serious corrosion and larger volume change may occur when the selected industrial calcination temperature is higher than 1000 ºC. Thus, the huge amount of reaction products formation and expansion may lead to a local stress increase and the refractory degradation.

The morphologies of reaction interfaces between cordierite and LNCM cathode materials after calcinations at different temperatures are presented in Fig. 3. It is seen in Fig. 3a and Fig. 3b that the bright white LNCM materials precursor and reaction products are almost independently distributed with cordierite grains at the temperature of 800 ºC and 900 ºC. However, as seen in Fig. 3c and Fig. 3d, the bright white reaction products precipitated along with the cordierite grains at 1000 ºC and the mutual infiltration of LNCM materials and cordierites happened at 1100 ºC.

It appears that the type of interactions changed and the extents increased when the temperature increases to 1000 ºC. These morphologies change are very consistent with the XRD (Fig. 2) and diameter expansion (Fig. 1). It could be inferred that liquid-solid interfacial reaction occurred at the temperature of 1000 ºC, and the amount of liquid formation facilitate the infiltration between cordierite and LNCM cathode materials.

The main reactions at the temperature at 800 ºC and 900 ºC are involved with the LNCM cathode precursor materials to form LNCM materials, although a little interfacial zone can be also detected at 900 ºC. As seen in Fig. 3, the bright white reaction products in Fig.3b are bigger and more round when compared with the same reaction products in Fig. 3a. This could be due to the solid-state reaction in LNCM cathode materials to form LNCM with the increase of the temperature. From the above results, it can be concluded that some LNCM materials precursor reacted with cordierite grains at the temperature of 800 ºC and 900 ºC and not much reaction products formed during this temperature range due to the main reaction type of slower solid-state. When the temperature was raised to 1000 ºC, the interfacial reactions between LNCM materials and cordierite were fully carried out through liquid-solid infiltrations, and a large area of liquid formation lead to the dissolution of cordierite grains. Moreover, the low density products of $LiAlSiO_4$ formed at the temperature above 1000 ºC may lead to the expansion, increase the local stress of the cordierite containing saggar matrix materials during recycles of calcinations-cooling procedure, and accelerates the spalling of the saggars.

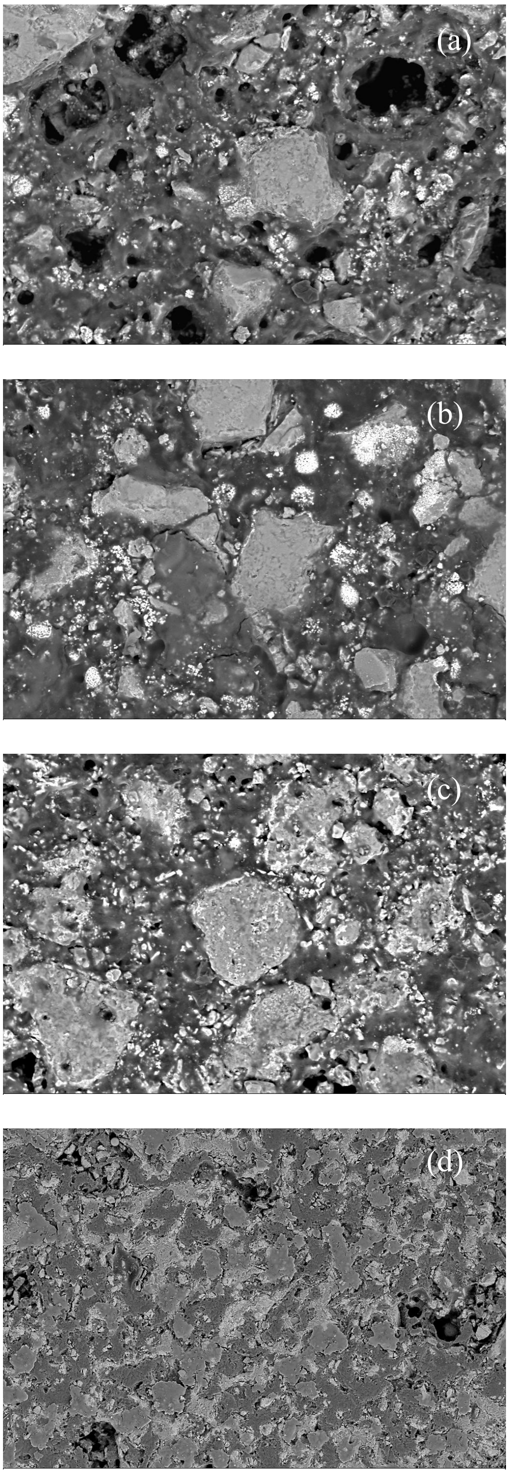

Fig. 3: Backscattered scanning electron micrographs of the polished sample surface of the mixtures of LNCM precursor and cordierite calcined for 6 h at 800 ºC (a), 900 ºC (b), 1000 ºC (c) and 1100 ºC (d).

CONCLUSIONS

The interfacial reactions between cordierite and Li-ion battery cathode materials were studied at the temperature range from 800 ºC to 1100 ºC. The extent of these reactions greatly increased from 900 ºC to 1000 ºC, and a large amount of products formation lead to the expansion and the local stress increase in refractory materials, facilitating the degradation of saggar materials. Therefore, using the cordierite containing saggars to calcine LNCM materials at the temperature above 1000 ºC could be the challenge.

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