Mobility-Revolution: Refractory Saggars for Calcination of Ternary Cathode Materials

A.-L. Schäfer, V. Schönhof

The corrosion resistance against the ternary cathode material NCA for various refractory materials was investigated. For this purpose, a crucible test was modified to fit the requirements during the calcination of NCA. To examine the long-term resistance of the ceramic materials, the crucible test with a mixture of NCA precursor and lithium carbonate was run six times at 1000 °C for 20 h. The reaction products were detected by X-ray diffraction analysis to get a better understanding of the reaction mechanisms taking place during corrosion. The results of the crucible test show different effects of corrosion on the various refractory materials. Raw mullite and silicate-bonded silicon carbide are characterised by heavy reactions with the battery material. Within magnesium aluminate spinel crucibles is an infiltration and an intense sticking of the NCA powder noticeable. Cordierite-mullite samples develop an amorphous corrosion layer, which slowly separates from the raw material. The best performance during the crucible test was achieved by an improved mullite-containing material. It forms a dense corrosion layer, which is not spalling or separating from the raw material. Beyond that no further infiltration of the material is visible.

1 Introduction

The automotive industry is changing to attain the global aim of emission-free mobility. In the last few years, the ratio of electric driven vehicles is constantly growing, which results in a booming battery industry.

The most used battery technology for electric vehicles is the Lithium Ion Battery (LIB). Ternary materials such as NMC ($Li_{m-n}(Ni_xMn_yCo_{1-x-y})O_2$) and NCA ($Li_{m-n}(Ni_xCo_yAl_{1-x-y})O_2$) are commonly used for the cathode of LIBs for electric vehicles. These materials are usually prepared through solid-state reactions at temperatures between 500–1000 °C [1, 2].

Refractory saggars are necessary for this calcination process (Fig. 1). Due to the low thermal expansion coefficient, good hot modulus of rupture, and low cost, saggars are commonly manufactured from cordierite-mullite materials. These show severe damage in consequences of corrosion after a few sintering cycles, which results in periodic replacing of the saggars and contamination of the cathode materials. To avoid these disadvantages, a high corrosion resistance against battery materials is a key property of new saggar materials.

Fig. 1 Example of stacked saggars produced by STEULER-KCH

In this paper, the corrosion resistance of common saggar materials and other interesting refractory materials of Steuler were investigated (Tab. 1).

Tab. 1 Chemical composition of the investigated materials

Saggar Material	Mullite	Cordierite Mullite	Silicon Carbide	Magnesium Aluminate Spinel
Chemical Analysis [mass-%]				
SiO_2	20	50	5	–
Al_2O_3	75	35	2	70
MgO	–	8	–	30
SiC	–	–	92	–

For ranking the materials in relation to their corrosion resistance a modified and repeated crucible test, also called cup test, was implemented, which reflects the requirements during the calcination. In addition to the crucible test, the reaction products between the potential saggar materials and the lithium-carbonate containing precur-

Anna-Lena Schäfer, Viktor Schönhof
STEULER-KCH GmbH
56203 Höhr-Grenzhausen
Germany

https://linings.steuler.de/en/home.html

Corresponding author: A.-L. Schäfer
E-mail: anna-lena.schaefer@steuler-kch.de

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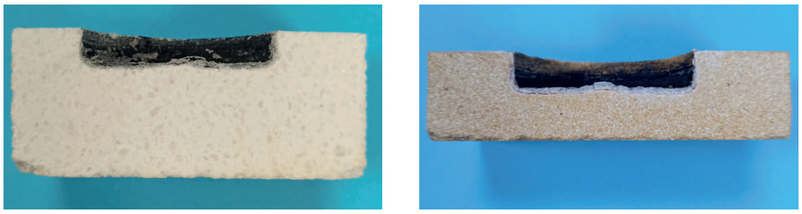

Fig. 2 a–b **Mullite (a, left) and cordierite-mullite (b) crucible after six cycles of the crucible test**

Fig. 3 a–b **Silicon carbide (a, left) and MA-spinel (b) crucible after six cycles of the crucible test**

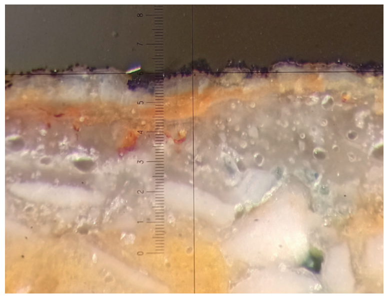

Fig. 4 **Reaction layer of the cordierite-mullite material due to corrosion of the NCA-precursor mixed with lithium carbonate**

sor were investigated by X-ray diffraction analysis.

2 Experimental

2.1 Experimental materials

The investigated refractory materials are mullite, cordierite-mullite, silicate-bonded silicon carbide, and Magnesium Aluminate spinel (MA-spinel). Except for the MA spinel, all listed materials are established refractory materials by STEULER. The sample of MA spinel material was developed by the experienced R&D team.

2.2 Crucible test

This paper focuses on the corrosion resistance against a mixture of NCA precursor and lithium carbonate of different refractory materials at 1000 °C. Crucible tests are state-of-the art for testing the resistance against different corrosive media. A crucible test adapted to the requirements of the calcination was implemented. The 10 mm deep crucibles (diameter: 40 mm) were filled with 5 g of a mixture of NCA precursor and lithium carbonate. Afterward, the crucibles were treated at 1000 °C for 20 h. The cut samples can be microscopically observed after the crucible test.

To evaluate the long-time resistance of the materials, the test was repeated six times with the same crucible. Conclusions about suitability for this application can be drawn by comparing the appearance of the formed corrosion layers of the different materials.

2.3 Reaction mechanism test

For a better understanding of the reaction mechanisms taking place during corrosion, NCA precursor and lithium carbonate were mixed with crushed particles of the ceramic materials. By adding temporary binders to the mixture, it was possible to form cylindric samples by dry pressing. After sintering the samples at 1000 °C for 40 h, they were crushed, and the mineralogical composition could be detected via X-ray diffraction analysis.

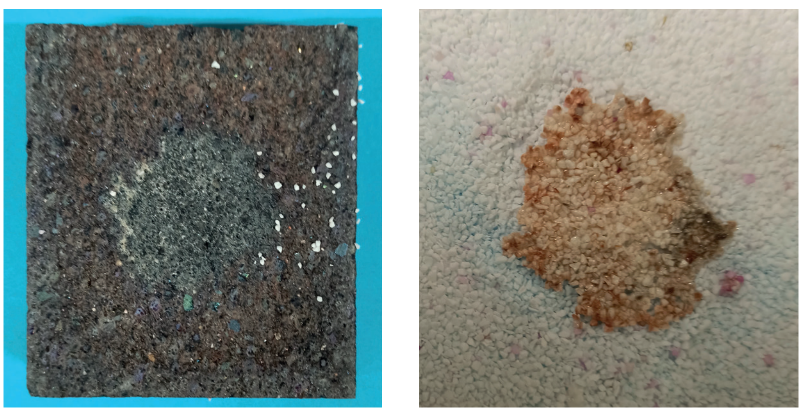

Fig. 5 a–b **Packed bed under the silicon carbide crucible after cycle 4 (a, left), and bottom of the silicon carbide crucible after cycle 4 (b)**

3 Results

3.1 Crucible test

The samples were cut and observed after six cycles of the modified crucible test (Fig. 2 a–b and Fig. 3 a–b). Each material showed a formation of a corrosion layer; however, the extent of the layer and its damage to the ceramic body varies from material to material.

The mullite crucible already shows severe structural spalling of the reaction layer after three cycles of the crucible test. After the last cycle an approx 1 mm-thick corrosion layer was found on the bottom of the crucible (Fig. 2 a). This reaction layer has a loose porous structure.

Contrary to the observations of the mullite material, the cordierite-mullite crucible did not show structural spalling of the corrosion layer. However, there is also a thick reaction layer due to the corrosion of the cathode material (Fig. 2 b). The reaction layer appears to be dense and still firmly connected to the crucible, although a separation between the corrosion layer and the raw material is already visible. By microscopically observing a polished section of the reaction layer after one cycle of the crucible test a formation of an amorphous reaction product can be discovered (Fig. 4).

The silicon carbide sample shows the most severe reactions during the crucible test. The packed bed, on which the samples

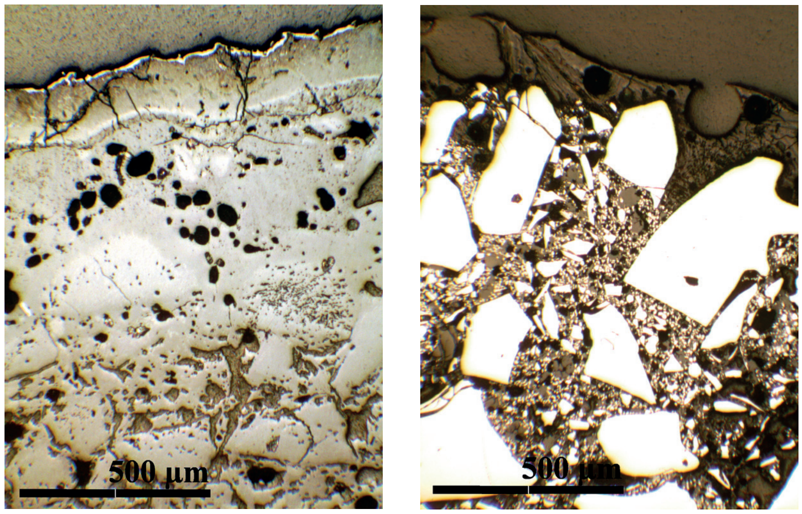

Fig. 6 a–b Polished sections of the cordierite-mullite (a, left) and silicon carbide material after one cycle of the crucible test (b)

are placed in the furnace, shows reactions under the silicon carbide crucible after three cycles (Fig. 5 a–b). It seems like a liquid leaked through the silicon carbide sample and was able to harden during furnace cooling. This reaction intensifies during the following cycles. The inside of the crucible also shows reactions due to corrosion. Besides some spalling of the crucible surface, a strong formation of reaction products is seen at the sides of the crucible. The silicon carbide material shows an infiltration around the crucible, which happened to be up to 8 mm deep (Fig. 3 a).

The MA-spinel material showed a 5 mm deep discoloration due to infiltration (Fig. 3 b). Above a thick reaction layer can be seen. During the repeated crucible test the NCA powder is always intensely sticking to the MA-spinel crucible and can hardly be separated. The residue of the NCA material builds up the thick discovered layer.

Fig. 6 a shows the reaction layers within the cordierite-mullite sample. The structure can be divided into three different layers. The first layer is the uppermost layer. It appears dense and includes cracks, which traverse vertically through the whole layer and spread horizontally at the separation to the second layer.

An amorphous phase with some residual mullite grains and spherical seeds forms the second layer. There is no cordierite matrix left in this layer. A smooth transition is seen between the second and the third layer. Raw cordierite-mullite material is found in the third layer. The first and second layers add to a 650 µm thick corrosion layer after one cycle of the crucible test.

The silicon carbide sample can be divided into two layers. Fig. 6 b shows the raw material of the silicate-bonded SiC body. It contains fired clay and SiC grains of different sizes. Some cristobalite formations can be found in the mullite matrix. The corrosion layer sits on top of the raw material and includes neither small SiC particles nor the mullite matrix. Just some bigger SiC grains reach into the layer of the corrosion product. This layer contains spherical seeds and cracks.

A crucible of an improved mullite-containing material shows much less severe reactions in consequence of the corrosion of the cathode material (Fig. 7). After six cycles of the crucible test a 1 mm thick corrosion layer can be detected. This layer appears dense and mechanically stable. No spalling of the surface was detected during the repeated crucible test. There is also no separation between the corrosion layer and the raw material nor infiltration of the body seen.

Fig. 7 Improved mullite-containing crucible after six cycles of the crucible test

3.2 Reaction mechanism test

The X-ray diffraction analysis of the mullite and cordierite-mullite sample lists in Tab. 2 the mineral phases after the reaction mechanism test:

The sample of mullite, NCA-precursor, and lithium carbonate contains the mineral phases mullite, corundum, a lithium aluminate, eucryptite, and various nickel-containing spinel phases after heat treatment at 1000 °C for 20 h.

Out of the listed phases mullite and corundum come from the raw material. On the other hand, the formation of lithium aluminate and eucryptite results from a reaction between the lithium carbonate and the mullite product. Nickel-containing spinel phases emerge through reactions of nickel ions with mullite, where nickel ions occupy the tetrahedral position.

Indialithe and nickel-containing indialithe are the main components of the cordierite-mullite sample after the reaction mechanism test. Indialithe is the high-temperature form of cordierite and is found instead in almost every so-called cordierite product. During the reaction, nickel ions substitute 6 % of the magnesium ions. Mullite, NiO, lithium feldspar, spodumene, and an X-ray amorphous phase are declared as secondary components. Mullite comes from the raw material, whereas lithium feldspar, and spodumene result from a reaction between lithium carbonate and the crucible. Nickel-containing spinel phases, forsterite, and a magnesium nickel-containing olivine phase are detected in traces. Nickel ions join the structure of the olivine and spinel phase in tetrahedral positions, while in one detected spinel phase they also occupy the octahedral position, which leads to a mixed structure between normal and inversed spinel structure.

4 Discussion

The reaction of mullite with lithium carbonate can be described as follows:

(1) $$Li_2CO_3 \rightarrow Li_2O + CO_2$$

(2) $$Al_6Si_2O_{13} + 3\ Li_2O \rightarrow 2\ LiAlSiO_4 + 4\ LiAlO_2$$

After the thermal decomposition of lithium carbonate, the formed lithium oxide can react with mullite. By calculating the theoretic

Tab. 2 Mineral analysis of the mullite and cordierite-mullite samples after the reaction mechanism test

Raw Material	Mullite	Cordierite Mullite
Mineral Composition		
Main components	Mullite	Indialithe Ni-containing Indialithe
Secondary components	Corundum Lithium aluminate (γ-$LiAlO_2$) Eucryptite (β-$LiAlSiO_4$) Various spinel phases	Mullite NiO Li-feldspar ($LiAlSi_3O_8$) Spodumene ($LiAlSi_2O_6$) Amorphous phase
Trace components	–	Various spinel phases Forsterite Mg–Ni-containing olivine

Tab. 3 Thermal expansion coefficient (× 10^{-6} K^{-1}) of mullite, lithium aluminate ($LiAlO_2$), and eucryptite respectively

Material	Mullite	Lithium Aluminate	Eucryptite
Thermal expansion coefficient	5–7	a-axis: 7 c-axis 15	a-axis: 7,8 c-axis: –17,5

Tab. 4 Comparison of the cation diameter [pm] of Mg^{2+}, Ni^{2+}, Co^{2+}, and Mn^{2+} respectively

Ion [Coordination Number 4]	Cation Diameter	Deviation to Mg^{2+} [%]
Mg^{2+}	57 pm	–
Ni^{2+}	49 pm	14
Co^{2+}	56 pm	2
Mn^{2+}	66 pm	16

expansion of volume for this reaction a potential cause for the severe spalling of the crucible surface was discovered.

The reaction to eucryptite and lithium aluminate comes along with a volume expansion of 45 vol.-%, which can destroy the structure of the mullite product. Furthermore, the thermal expansion coefficients of the newly formed products don't match these of the mullite material (Tab. 3) and induce more stress to the crucible surface during the following cycles.

The vitrification inside the cordierite-mullite material occurs below the maximum service temperature. By reacting to Li-feldspar and spodumene a lowering of the melting temperature is imaginable. The reactions of nickel ions with the ceramic material are limited to the formation of spinel phases and substitution reactions. The incorporation of MnO is known to barely change the lattice parameter of MA-spinel [3].

Due to matching ion diameters (Tab. 4), the substitution reactions of nickel ions in indialithe should not significantly change the lattice parameters and therefore should not decrease the corrosion resistance by destroying the structure of the material. The incorporation of nickel ions in an octahedral position in spinel is caused by its 3d electron configuration, which leads to mixed structures of nickel-containing spinel phases [4].

By comparing the cation diameters, cobalt ions should also be able to substitute Mg ions, which was not detected during the reaction mechanism test.

5 Conclusion

The results of the implemented crucible and reaction mechanism test showed different suitability for the application as saggar material for calcination of NCA cathode material. While the reaction with lithium ions forms various lithium-containing aluminates and aluminosilicates, which can destroy the structure of the corrosion layer, the nickel ions tend to form spinel phases and substitute mainly magnesium ions in different structures. It is a necessity to choose a saggar material, that is resistant against lithium-ion attack, to improve the corrosion resistance during NCA calcination.

Magnesium aluminate spinel showed intense sticking of the NCA material to the crucible. Because of this unwanted behaviour, the magnesium aluminate spinel is assessed as not suitable for this application.

Due to severe reactions with the battery material during the repeated crucible test, the silicate-bonded silicon carbide is also no reasonable choice as a saggar material for the calcination of NCA material.

The mullite material shows severe spalling due to a volume expansion during the reaction with lithium ions and mismatching thermal expansion coefficients of the educt and the products. This spalling would cause massive contamination of the NCA product, which would lead to subsequent steps after the calcination. A vitrification takes place inside the surface layer of the cordierite-mullite body due to reactions with lithium carbonate. After the crucible test, no severe spalling was detected; however, the cracks between the corrosion layer and the raw material seams to cause spalling during further cycles and the vitrification can decrease the mechanical properties of the saggar.

The best corrosion resistance showed the improved mullite-containing material. Although a formation of a thin corrosion layer was observed, the corrosion layer seemed firmly connected to the raw material underneath, and no severe spalling took place during the crucible test.

Considering this, the improved mullite-containing material seems to be the best fit as a saggar material for the calcination of NCA cathode material.

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