



Short communication

Research activities in Shanghai Institute of Ceramics, Chinese Academy of Sciences on the solid electrolytes for sodium sulfur batteries

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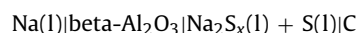
ABSTRACT

This paper presents the research and development of β'' -Al₂O₃ ceramic electrolytes for sodium sulfur battery applications in the Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS). The process to prepare large size β'' -Al₂O₃ ceramic tubes is described. Composite electrolytes with ZrO₂ as second phase additives are introduced. The strengthening and toughening effects of the second phase are significant. The results show that high quality β'' -Al₂O₃ ceramic electrolytes with diameter as large as 60 mm and length of 500 mm are successfully produced. The composite of β'' -Al₂O₃ and tetragonal ZrO₂ displayed much better mechanical properties than the pristine β'' -Al₂O₃ ceramics.

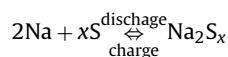
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1. Introduction

Details of the sodium sulfur batteries were first released in 1966 by Ford Motor Company. Sodium sulfur battery is one of the most promising candidates for energy storage applications developed since 1980s [1–5]. The battery as expressed below is composed of sodium anode, sulfur cathode and beta-Al₂O₃ ceramics as the electrolyte and separator simultaneously.



It works based on the reversible electrochemical reaction between sodium and sulfur and the formation of sodium polysulfide during charging and discharging processes as described in the following reaction:



The sodium sulfur battery exhibits high power and energy density, temperature stability, more over low cost because of its abundant low cost raw materials and suitability for high volume mass production [2–4]. Great achievements have been made during the last two decades to develop the sodium sulfur battery for the applications in stationary energy storage. The batteries

have been applied in various ways such as load levelling, emergency power supply and uninterruptible power supply. The markets covered industrial, commercial owners and wind power generating systems, etc. The research work on sodium sulfur battery in China is dated back to 1970s, but since 1980, SICCAS has become the only Chinese institution engaged in sodium sulfur battery research. Sodium sulfur cells with different capacities in the range of 20–650 Ah were made by the institute. The cells demonstrated favorable cycling stability with life over 1000 cycles. A 6 kW sodium sulfur battery unit made up of the 30 Ah single cells was ever assembled for EV applications in SICCAS. Beta-Al₂O₃ ceramics were applied as solid electrolytes for the sodium sulfur battery. Now the researches on sodium sulfur battery are going on in the institute, especially for stationary energy storage applications. In this paper, we will review the main research activities in SICCAS on the solid electrolytes for sodium sulfur battery.

2. Basic description of β'' -Al₂O₃ electrolyte

Sodium sulfur battery applies sodium and sulfur as the anode and cathode, respectively, and beta-Al₂O₃ ceramic as both the electrolyte and the separator simultaneously. Tubular sodium central geometry is the most favorable configuration for the design of sodium sulfur battery which allows the volume change of the electrodes during cycling and minimizes the sealing area and therefore becomes the popular design for practical batteries. Fig. 1 shows a typical tubular cell design with a central sodium electrode and

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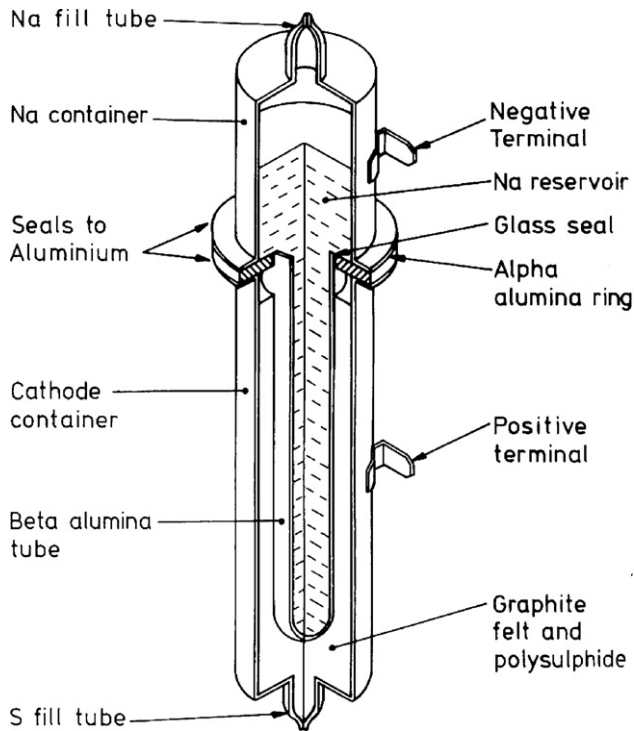


Fig. 1. Schematic illustration of a central sodium electrode tubular Na-S cell with sodium reservoir [5].

a sodium reservoir [5], as seen, different kinds of materials are involved in the tubular design, they are mainly cathode electrode materials, i.e., composite of sulfur, polysulphide and graphite felt, α - Al_2O_3 ceramic insulating ring to separate the cathode and anode compartments, sealing materials to connect various parts of the cell, for example, glass for sealing the electrolyte ceramics and the insulating ring, metal for sealing the current collector and the electrode compartments. Among all the materials involved, the β'' - Al_2O_3 ceramic tube, acted as an electrolyte and separator, is the most difficult and key part. β'' - Al_2O_3 is one of the sub-groups of sodium aluminates with layer type structure composed of tightly packed spinel blocks and loosely packed Na–O slabs which accommodate the Na^+ ions and afford them fast ion transfer channels as shown in Fig. 2 [6]. Li^+ and Mg^{2+} are two most popular doping ions to stabilize the β'' - Al_2O_3 , the ideal compositions are $\text{Na}_{1.67}\text{Al}_{10.33}\text{Mg}_{0.67}\text{O}_{17}$ for Mg^{2+} dopant and $\text{Na}_{1.67}\text{Al}_{10.67}\text{Li}_{0.33}\text{O}_{17}$ for Li^+ dopant [6].

The main factor determining cell performance is the internal resistance and the main contributor to this is the ceramic electrolyte. Sodium sulfur battery usually works at the temperature ranging between 300 and 350 °C, at which sodium and sulfur as well as the reaction product polysulfide exist in liquid state, which affords high reactivity of the electrodes. Moreover, the β'' - Al_2O_3 ceramic electrolyte exhibits satisfactory sodium ion conductivity at a moderate temperature. Although the cell resistance can be reduced by increasing the temperature of operation, there is little advantage in operating at higher temperature [6]. Therefore, properties of beta- Al_2O_3 ceramic electrolytes are most essential factor to determine the overall performance of the batteries.

Typical resistivity of β'' - Al_2O_3 at 300 °C is 5–6 Ω cm. In addition to electrical properties, mechanical performances such as flexural strength and crack toughness are also essential for β'' - Al_2O_3 electrolytes. In order to confirm the high quality of the sodium sulfur battery, the β'' - Al_2O_3 ceramic electrolytes should meet the following requirements: (1) high sodium ion conductivity, (2) low

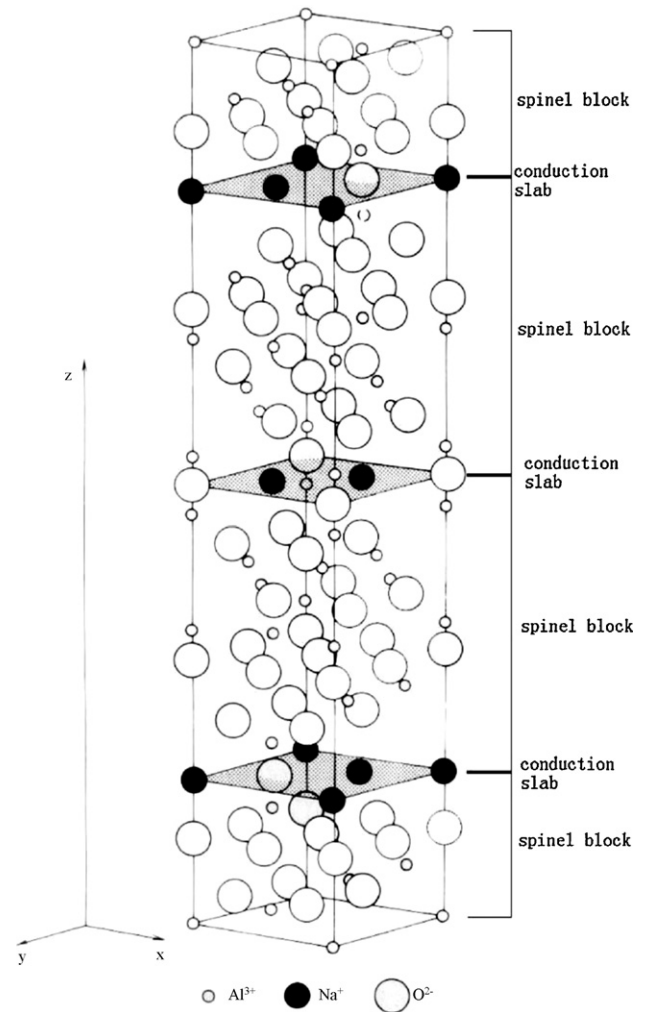


Fig. 2. Perspective drawing of the idealized structure of β'' - Al_2O_3 .

electronic transference number, (3) high relative density and (4) high mechanical strength.

3. Research work in SICCAS

3.1. β'' - Al_2O_3 ceramic electrolyte

As mentioned above, SICCAS has become the only Chinese institution engaged in sodium sulfur battery research since 1980. Systematic investigations on β'' - Al_2O_3 ceramic electrolytes were carried out in the institute. Ceramic tubes with homogenous

Table 1
Properties of β'' - Al_2O_3 ceramic tubes prepared by SICCAS

Property	Value
Outer diameter (mm)	10–60
Length (mm)	100–500
Thickness (mm)	1.0–1.5
Chemical composition (wt%)	Na_2O : 9.0, Li_2O : 0.72, Al_2O_3 : balance
Relative density (%)	>99
Relative β'' - Al_2O_3 phase content (%)	>99
Matrix grain size (μm)	1–5
Sodium ion resistivity at 300 °C (Ω cm)	5–6
Bending strength (MPa)	250 \pm 26

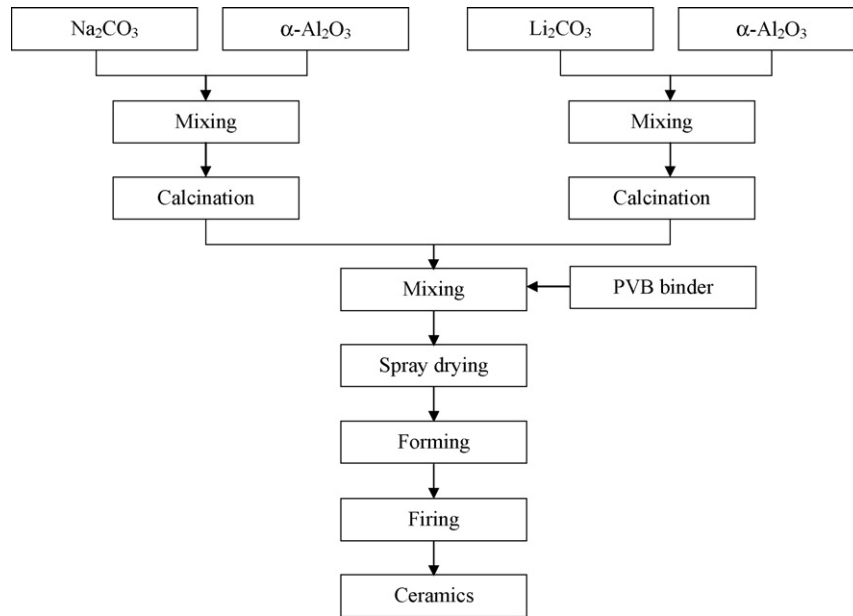


Fig. 3. Schematic illustration of double zeta process.

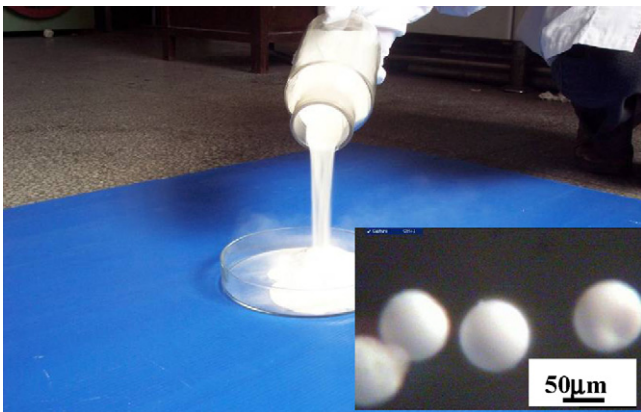


Fig. 4. Precursor powders with good fluidity and spherical particle morphology.

microstructure, favorable electrical and mechanical properties were fabricated based on a double-zeta powder process as illustrated in Fig. 3 [7].

Different from the processes adopted by NGK [2], the precursors Li-zeta and Na-zeta were first synthesized separately in order to realize the homogenization of the small amount of the lithium content in the powders and the final ceramic products. The experimental results indicated that the double zeta process produced more homogeneous green powders than normal solid state reaction process because of the pre-dilution for the minor component lithium in the major component alumina. Isostatic pressing was chosen as the main route to form the ceramic green tubes, therefore powders with high fluidity are necessary to guarantee the quality of the green tubes. Fig. 4 demonstrated the good fluidity of the powders prepared by slurry spray drying process, the particles of the spray-dried powders possess an average size of 50 µm. Fig. 5 illustrated the ceramic tubes with diameters of 150 and 600 mm, respectively, employed in the sodium sulfur batteries for electric vehicle application and for energy storage application. Table 1 listed the basic properties of the ceramic tubes prepared in this institute.

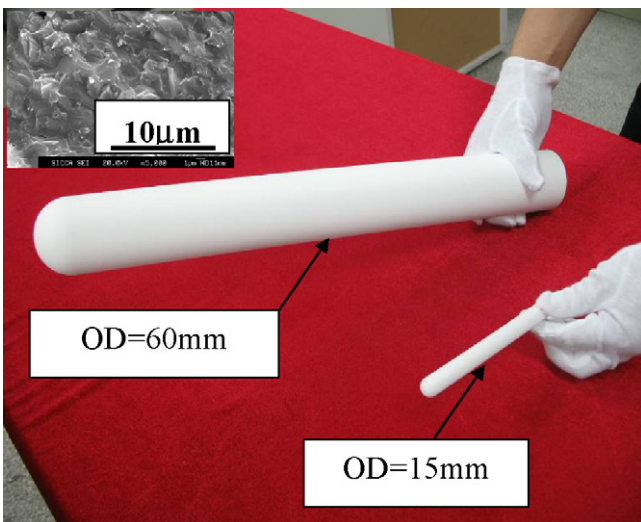


Fig. 5. Ceramic tubes with different sizes.

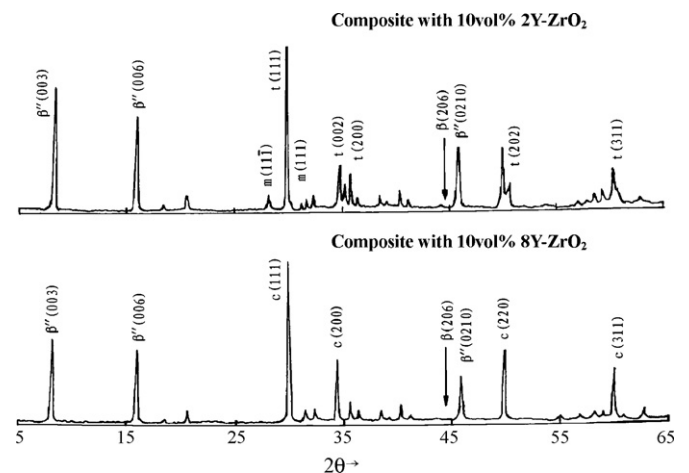


Fig. 6. XRD patterns of β'' - $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite.

3.2. β'' - $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite electrolyte

It has long been known that under certain conditions, the β'' - Al_2O_3 solid electrolyte undergoes strength degradation which manifests itself in the form of cracks filled with liquid sodium. The sodium filled cracks propagate through the thickness of the ceramic electrolyte tubes and result in the failure of the battery. It was deduced that the current density above which the degradation of the ceramic separator occurs is proportional to the fourth power of the K_{IC} (the fracture toughness) [8]. Therefore, improvement of the mechanical strength and K_{IC} of the β'' - Al_2O_3 ceramics should lead to significant enhancement of the battery life. The transformation from tetragonal- ZrO_2 (t- ZrO_2) to monoclinic- ZrO_2 (m- ZrO_2) has been used successfully to toughen and strengthen many ceramic systems. It was also employed to β'' - Al_2O_3 by many laboratories [9–12].

To prepare the β'' - $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite, the precursor powders are prepared similar to the above procedures for the pristine β'' - Al_2O_3 ceramics unless the addition of nano- ZrO_2 powders in different weight ratios to the zeta powders. Fig. 6 shows the XRD patterns of the sintered composite ceramics with 10 vol.% of 2Y and 8Y ZrO_2 , respectively, it is seen that all the peaks are indexible to β'' - Al_2O_3 and ZrO_2 phases, which demonstrated the chemical compatibility between the two components. The chemical compatibility is also certified by the high resolution of the composite (Fig. 7), it is seen that no any new compounds is found from the interface of the β'' - Al_2O_3 and ZrO_2 particles.

Fig. 8 shows the microstructure of composites containing different kinds and contents of ZrO_2 , as seen, the microstructure of the β'' - Al_2O_3 is greatly improved by the addition of the second inert ZrO_2 phase (white area). Abnormal growth of the β'' - Al_2O_3 particles as displayed in Fig. 8(a) has been avoided while 10 vol.% of the ZrO_2 is added, no matter what kind of phase it is. Table 2 lists the mechanical and electrical properties of typical composites. As observed, the

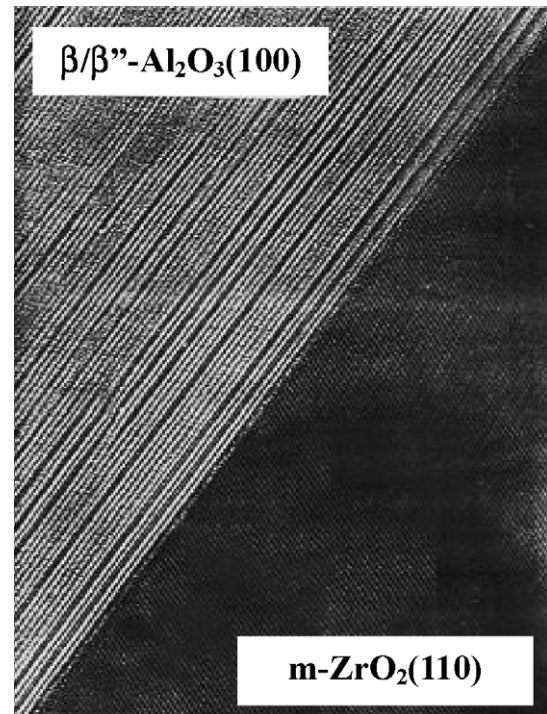


Fig. 7. TEM image of β'' - $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite.

strengthening and toughening effect of ZrO_2 is significant, while the electrical properties is comparable to that of the pristine β'' - Al_2O_3 . The effect in the t- ZrO_2 containing composite is even more remarkable than the c- ZrO_2 containing composite. As analyzed previously, microcrack toughening and crack deflection (as seen in

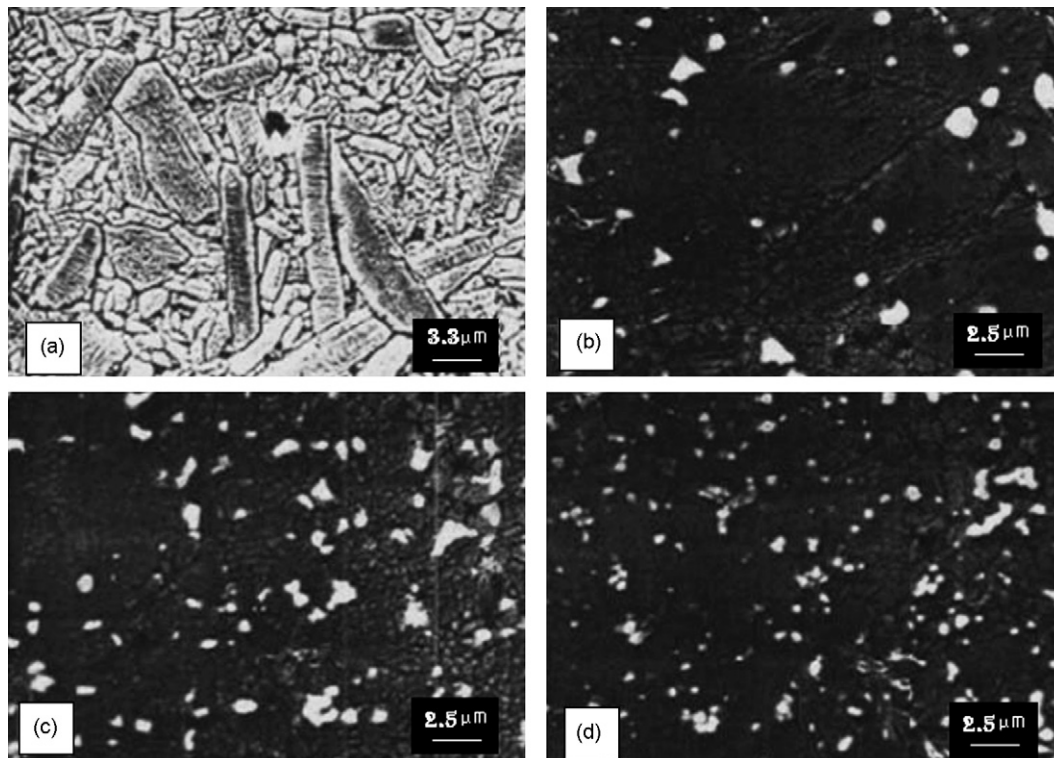


Fig. 8. SEM microstructure of the pristine β'' - Al_2O_3 (a) and its composites with additives, 5 vol.% 8Y- ZrO_2 (b), 10 vol.% 8Y- ZrO_2 (c) and 10 vol.% 2.5Y- ZrO_2 (d).

Table 2
Mechanical and electrical properties of β'' - $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite ceramics

ZrO ₂ in composite (vol.%)	Y ₂ O ₃ in ZrO ₂ (mol.%)	Bending strength (MPa)	Fracture toughness (MPa cm ^{1/2})	Resistivity at 300 °C (Ω cm)
0	/	250	2.3	5.7
10	2.5	278	3.1	9.3
15	2.5	314	3.4	9.8
20	2.5	330	3.7	11.0
15	6	270	3.0	9.8

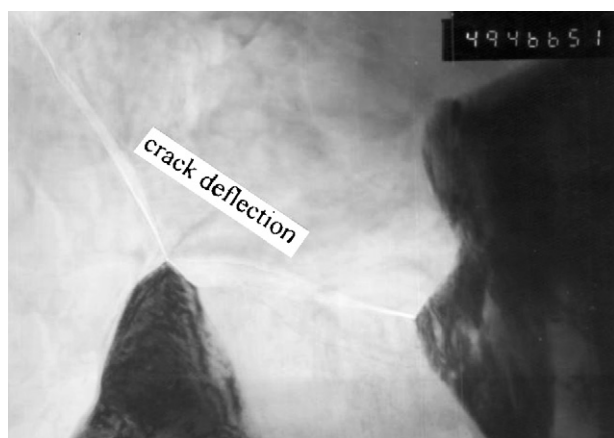


Fig. 9. TEM microstructure of a β'' - $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite ceramics, implying the crack deflection in the composite.

Fig. 9) mechanisms are attributed to the c- ZrO_2 containing composite, moreover, the t–m phase transformation mechanism is ascribed to the more significant toughening and strengthening effects of the t- ZrO_2 -based composites.

4. Conclusions

β'' - Al_2O_3 ceramic tubes of different sizes with favorable performance are prepared in the Shanghai Institute of Ceramics,

Chinese Academy of Sciences, they are successfully employed in sodium sulfur battery for EV and for energy storage applications. β'' - $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite ceramics are possible candidates for the fabrication of sodium sulfur battery with less degradation because of their improved mechanical strength and fracture toughness.

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