

Properties and morphology of doped polycrystalline Na- β'' -alumina electrolytes

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The effect of trace concentrations of metal oxides, Zn, Mg, Nb and Ge, on the intermediate temperature resistivity of Na- β'' -alumina electrolytes was investigated. The presence of the dopant oxides resulted in lowered resistivity values over the temperature range of 20 to 350°C. When the resistivities of the doped electrolytes were normalized to account for increased grain size relative to undoped samples, it appeared that the most effective additions for improving electrolyte conductivity were MgO and Nb₂O₅. The resistivity of the magnesia-doped samples at 170°C was as low as for that of the undoped electrolyte at 290°C, implying that magnesia doping of lithia-stabilized β'' -alumina electrolytes may improve the low temperature performance of β'' -alumina-based batteries.

1. Introduction

The power densities of intermediate temperature (150 to 250°C) batteries using tubular Na- β'' -alumina separators will most likely be limited by the resistivity of the solid electrolyte. It has been recognized for some time that as the temperature of secondary batteries based on Na- β'' -alumina electrolytes is lowered below 350°C, the intergranular resistivity becomes an increasingly important, and ultimately dominant component of the ohmic drop across the electrolyte [1–3]. Accordingly, the lowering of grain boundary resistance, either through manipulation of the ceramic microstructure or by addition of trace amounts of dopants prior to sintering, might lead to Na- β'' -alumina electrolytes more suited to intermediate temperature operation. Optimization of electrolyte conductivity should translate to an increase in power density achievable with intermediate temperature cells such as the sodium/Na- β'' -alumina/metal chloride [4], and sodium/Na- β'' -alumina/polyorganodisulfide batteries [5].

2. Experimental

Na- β'' -alumina specimens were fabricated from

commercial Na- β'' -alumina powders (Ceramtec, Inc., Salt Lake City, Utah) of nominal composition 90.40 wt% Al₂O₃, 8.85 wt% Na₂O, and 0.75 wt% Li₂O. A series of 100 g samples of the commercial Na- β'' -alumina powder was mixed with 0.2 wt% of one of the oxides of germanium, magnesium, niobium or zinc. The samples (doped and undoped) were subsequently ball-milled in acetone with 0.2 mm ZrO₂ balls, air dried, and filtered through 100 mesh sieves. The homogeneous powders were then cold uniaxially pressed at low pressure into disks of approximately 1 cm diameter by 0.5 cm thickness. The green bodies were finally hot-pressed two pellets at a time with one pellet composed of pure Na- β'' -alumina and the second pellet containing the impurity oxide. The green pellets were surrounded by boron nitride powder and were separated by tantalum sheets. The hot-press furnace was brought to sintering temperature at a heating rate of 29°C per minute, and the samples were densified at a temperature of 1450°C and a pressure of 5815 PSIA for a total of 30 min; the resulting ceramics all had relative densities in excess of 96% of theoretical density. The faces of the hot-pressed ceramic electrolytes were then polished to a mirror finish with successively finer grades of alumina powder and diamond paste. Blocking gold electrodes were subsequently sput-

tered onto both faces of the polished polycrystalline samples prior to analysis by impedance spectroscopy. Ionic conductivity measurements were performed in the frequency range of 1 Hz to 1 MHz with a Hewlett-Packard 3575 A gain/phase meter and a Hewlett-Packard 3312A function generator. All measurements were determined under an argon atmosphere in a quartz furnace, from approximately 130°C to 350°C. After analysis by ac impedance, the ceramic electrolytes were polished with diamond paste to 1 μm , and either thermally etched at 1400°C for 40 min or chemically etched with boiling H_3PO_4 . The microstructure of the etched electrolytes was examined by optical and scanning electron microscopy (SEM).

3. Results and discussion

The impedance spectrum of the doped and undoped Na- β'' -alumina disks displayed impedance spectra characteristic of the polycrystalline electrolytes. The equivalent circuit for the ceramic electrolytes can be described as shown in fig. 1, where the ionic current path involves the series resistance of bulk (intragranular) transport and grain boundary (intergranular) transport. This simplification of the electrical response of the electrolyte is useful for qualitative interpretation of conductivity trends.

The admittance spectra of the GeO_2 -doped electrolyte typifies the spectra of the doped and undoped samples; the spectrum over a range of temperatures is shown in fig. 2. As can be seen from the experi-

mental data, the low frequency arc attributed to the grain boundary resistivity is dominant at low temperatures, and decreases in magnitude with increasing temperature, until at temperatures above approximately 130°C, the time constants for the grain boundary and bulk relaxations are unresolvable. The admittance plots (fig. 2) indicate that the grain boundary resistance is about 5/6ths of the total resistance at 20°C and has diminished to 1/2 of the total resistance at 29°C.

Arrhenius plots of the total ionic conductivity for the Na- β'' -alumina ceramics are shown in fig. 3. As is evident from the graph, the total conductivity for all the doped samples was improved over the entire temperature range relative to the undoped Na- β'' -alumina samples. Notably, the total resistivity of the MgO doped samples at 170°C are approximately the same as for undoped β'' -alumina at 290°C. Assuming that the structural properties and chemical stability of the MgO doped samples are not compromised relative to the undoped samples, solid electrolyte batteries could operate at temperatures as low as 170°C with the same power loss across the electrolyte as cells using undoped electrolyte at 300°C.

As can be seen in fig. 3, the increase in the total conductivity was larger at lower temperatures where grain boundary effects are most important. The conductivities appear to merge at higher temperatures where grain boundary resistance should be minimal, and intragranular resistance should be the controlling feature for ionic transport. As described in table 1, the lowest resistivities over the entire temperature range were obtained for the ZnO-doped β'' -alumina polycrystals (MgO-doped electrolytes were slightly less resistive at 170°C).

Since Arrhenius plots of the conductivity data tend to converge at high temperatures, it would seem that the dopant effect is manifested in the grain boundary resistance. This is also likely in that the low concentrations of dopant cations are unlikely to cause appreciable changes in the bulk conductivity of the electrolyte. However, the trace amounts of dopants in the β'' -alumina samples also preclude detection of the impurities, even as precipitates at the grain boundaries [6]. Accordingly, the observed trends in the conductivity data are consistent with lowering of the grain boundary resistance, but this may be due

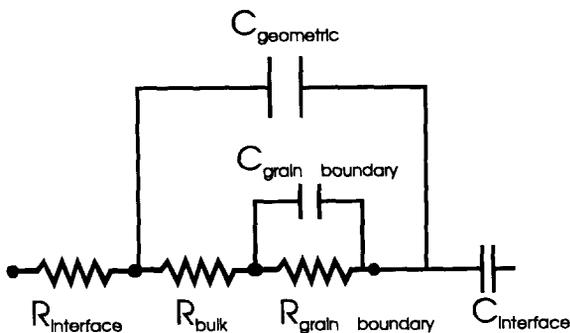


Fig. 1. Equivalent circuit for polycrystalline Na- β'' -alumina electrolytes.

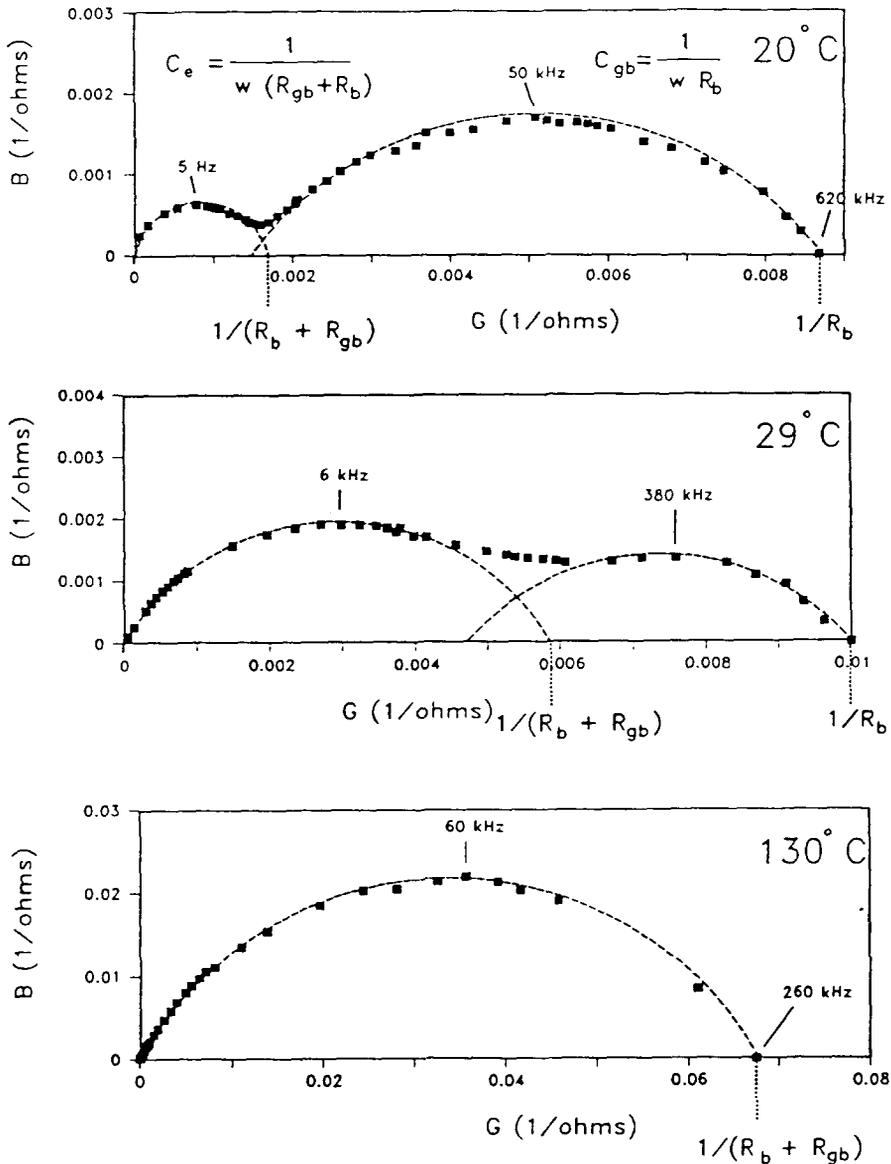


Fig. 2. Complex admittance spectrum for Na-β''-alumina electrolytes doped with 0.2 wt% GeO₂, as a function of temperature.

either to lowering of the activation energy for intergranular transport, or through morphological associated with the reduced number of grain boundaries that the mobile sodium ions encounter on transport through the polycrystals. It appears likely that both are true, since SEM micrographs confirm increased grain size upon addition of the dopant metal cations (fig. 4). As can be seen from the SEM pictures, the addition of trace amounts of dopants to the β''-alu-

mina powders gave rise to dramatic differences in the final microstructures of the hot-pressed ceramics. The lowered resistivities of the doped samples are certainly due in part to the increase of the average grain size of the electrolytes. The undoped β''-alumina electrolytes show the typical duplex microstructure consisting of small micron-sized grains and large needle-like grains (40–100 μm). The average grain size of the doped/undoped electrolytes

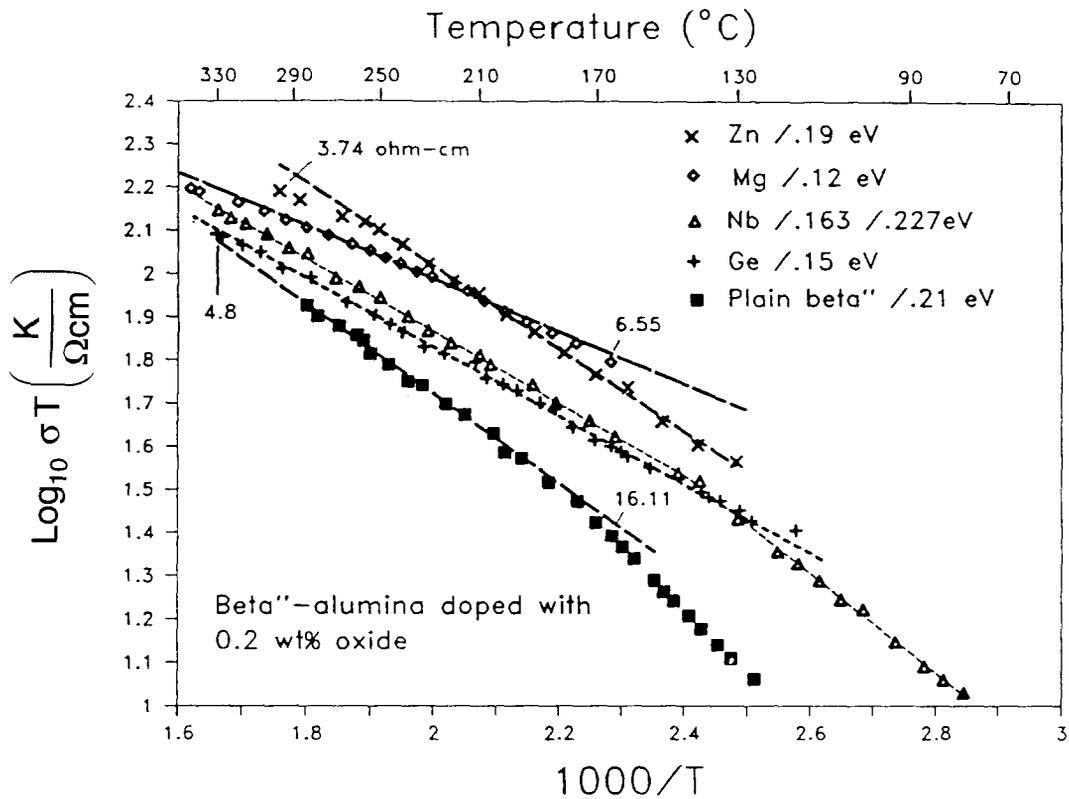


Fig. 3. Arrhenius plot of the total conductivity for polycrystalline Na-β"-alumina with and without dopant metal oxides.

Table 1
Total resistivities (ρ_t of doped/undoped samples (Ω cm)).

Temp. (°C)	Undoped β"-alumina	ZnO	MgO	Nb ₂ O ₅	GeO ₂
290	6.17	3.64	4.23	5.02	5.47
170	16.1	7.7	6.55	9.92	10.63

was determined by the lineal intercept method [7] (eq. (1)),

$$G = (1.56 \cdot L) / (M \cdot N),$$

where L = the total length of the line used, M = the magnification of the photomicrograph and N = the number of intercepts.

As indicated in table 2 the largest degree of grain growth was observed for the GeO₂ and ZnO doped samples (ZnO and MgO have also been used as stabilizers for the β"-alumina structure and can enter

the spinel blocks). In the case of GeO₂ doped β"-alumina, the average grain size is increased by approximately a factor of 10 relative to the undoped samples. Clearly, much of the improvement in low temperature resistivity for these samples can be attributed to increased grain size. It is likely that grain growth is due to the appearance of liquid phase sintering at or below the sintering temperature. In every case, the addition of dopant metal cations appears to have increased the average grain size of the electrolyte as well as improved the microstructural homogeneity of the hot-pressed electrolytes.

The resistivities of the doped β"-alumina electrolytes at 170°C samples can be normalized to reflect the expected resistivities in the absence of grain growth (relative to the undoped samples); a linear relationship between grain size and resistivity is assumed. As discussed earlier, at 30°C, the grain boundary resistance contributes to only 50% of the total resistance of the electrolyte. Using this as an

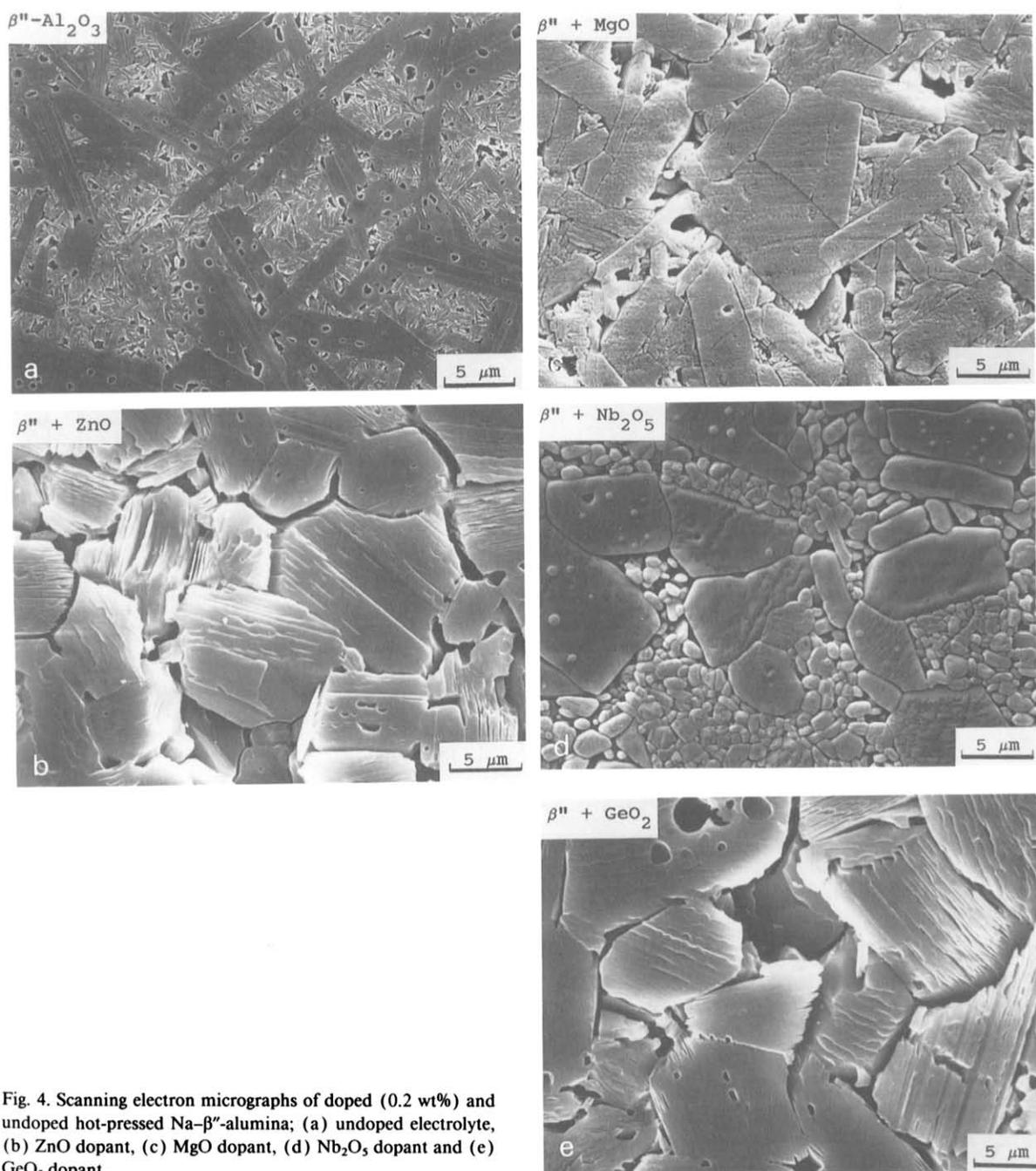


Fig. 4. Scanning electron micrographs of doped (0.2 wt%) and undoped hot-pressed Na- β' -alumina; (a) undoped electrolyte, (b) ZnO dopant, (c) MgO dopant, (d) Nb₂O₅ dopant and (e) GeO₂ dopant.

upper limit (clearly R_{gb} contributes less than 50% at 170 °C) the resistivities were normalized to the grain size observed in the undoped β' -alumina electrolytes.

The corrected total resistivities displayed in fig. 5

imply that additions of MgO and Nb₂O₅ appear to have the most beneficial effects on the electrical properties of doped β' -alumina electrolytes. In addition to reducing the observed resistivities (table

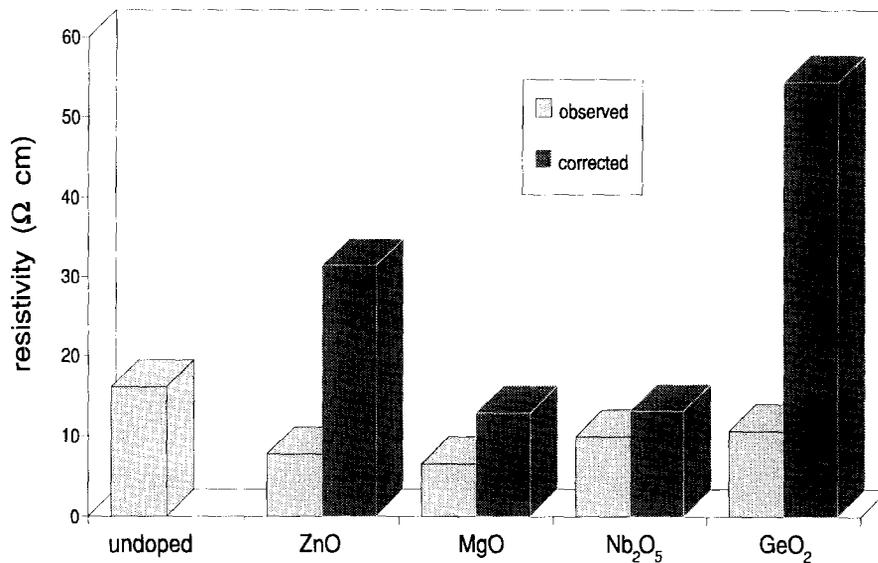


Fig. 5. Observed and normalized (for grain size) total resistivities for doped and undoped Na- β'' -alumina electrolyte at 170°C.

Table 2
Average grain size (μm) measured by lineal intercept method [7].

Undoped β'' -alumina	ZnO	MgO	Nb ₂ O ₅	GeO ₂
1.10	7.88	3.24	1.82	10.16

1) and corrected resistivities (table 3) of the electrolytes, these additives increased the homogeneity of the ceramic microstructure (fig. 4), possibly leading to improved mechanical properties. Even after correction for grain size, the MgO doped samples exhibited lower resistivities than the undoped samples at 170°C. Lowered grain boundary resistivity may be due to the presence of liquid reactant at or below the sintering temperature leading to dense boundary

Table 3
Total resistivities of doped samples normalized for grain size ^{a)}.
 $\rho_{\text{corr}} = 0.5 \cdot \rho_t [1 + (\text{grain size doped sample}/1.10)]$.

ZnO	MgO	Nb ₂ O ₅	GeO ₂
31.4	12.9	13.1	54.4

^{a)} Predicted resistivities of doped samples having average grain size of 1.10 microns.

conductivity. Since MgO is often used as a stabilizer for β'' -alumina, it is unlikely that doping the lithia-stabilized electrolyte with magnesia would adversely affect the chemical stability of the electrolyte.

4. Conclusion

The addition of low concentrations of metal oxides (ZnO, MgO, Nb₂O₅, and Ge₂O₅) to Li-stabilized β'' -alumina powders results in lowered resistivity values over the temperature range of 20 to 350°C. SEM studies of the fractured electrolytes indicated that in each case the grain size of the hot-pressed samples was increased as a result of the addition of the impurity metal oxide. When the resistivities of the doped electrolytes are normalized to account for increased grain size relative to undoped samples, it appears that the most effective additions for improving electrolyte conductivity are MgO and Nb₂O₅. The resistivity of the magnesia-doped samples at 170°C is as low as for that of the undoped electrolyte at 290°C, implying that MgO doping of lithia stabilized β'' -alumina electrolytes may improve the low temperature performance of β'' -alumina batteries. Additional benefits from dopant additions may be improved mechanical properties of ceramic electro-

lytes due to more homogeneous microstructures. The observed improvement in ionic conductivity over the temperature range of 100–250°C may be quite useful to intermediate temperature cells that are currently under investigation, such as the sodium/metal chloride and sodium/polyorganodisulfide cells.

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