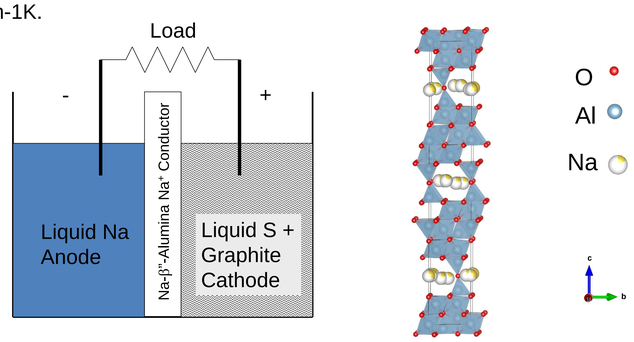
High performance Na-β”-alumina electrolyte doped with iron oxide

Leila Ghadbeigi, Alex Szendrei, Taylor D. Sparks, and Anil Virkar
Department of Materials Science and Engineering – University of Utah

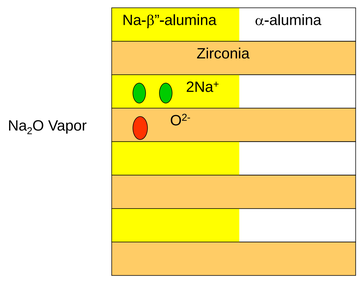
Abstract

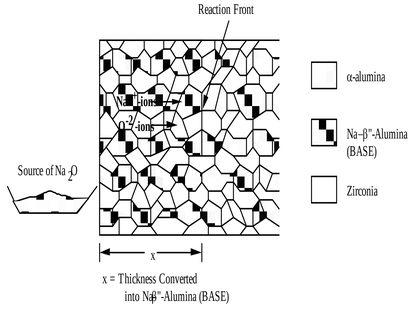
- This work presents the synthesis and characterization of an optimized high performance Na-β”-alumina as an electrolyte for sodium sulfur batteries.
- The material was synthesized by doping α-alumina with a small portion of iron oxide in order to increase electrical conductivity.
- Results indicate full dissolution of the hematite into the α-alumina structure.
- Ionic conductivity measured by electrochemical impedance spectroscopy.
- The bulk conductivity of the converted sample exhibited Arrhenius behavior with an activation energy of 0.20 eV and a pre-exponential factor of 421 Ω-1cm-1K.



Background & Objective

- Na-β”-alumina is the best Na^+ ion conductor. It is used as an electrolyte in sodium-sulfur and ZEBRA batteries, alkali-metal thermal to electric converters.
- The structure consists of three spinel blocks separated by a conduction plane.
- The vapor phase process consists of :
  - Fabrication of a two phase sintered composite of α-Al_2O_3+YSZ.
  - Exposing the composite to a vapor of Na_2O by packing in a powder of Na-β”-alumina and heat treating at a temperature between ~1250◦C and 1400◦C.
  - the coupled diffusion of $2Na^+$ through the Na-β”-alumina and O^{2-} through YSZ, viable the conversion.
- Recent studies of β and β”- alumina doped with iron indicate a small increase in electrical conductivity.
- The goal of this study was to synthesize a substitutional solid solution of iron doped β”-alumina utilizing a vapor phase method. The product will be a mixed ionic electronic conductor that improves electrochemical performance of the device and eliminates delamination.



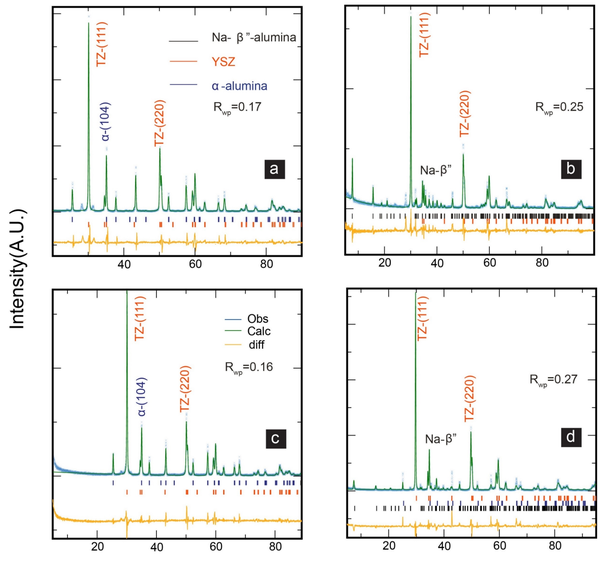


Methods

- A powder mixture of 70 vol.% (95 mol.% α -Al_2O_3 + 5 mol.% Fe_2O_3) and 30 vol.% TZ-3Y was prepared by ball milling
- The powder was compacted and sintered at 1450ºC for 3hours
- Disk was placed in packing powder and heat treated at 1250ºC for 20 hours.
- X-ray diffraction patterns were obtained using Cu Ka radiation on a Phillips X'Pert X-ray diffractometer. Lattice parameters were obtained using GSAS software with Rietveld refinement.
- Electrochemical impedance spectroscopy was performed using 4 probe method in the range of 100 Hz to 1 MHz. the temperature varied from 200ºC to 500ºC.

Results

- As seen in the table, the Fe-doped α-Al_2O_3 has slightly larger lattice parameters than the undoped α -Al_2O_3 consistent with the higher ionic radius of Fe^{3+} compared to Al^{3+}.
- For Fe-doped α-Al_2O_3, lattice parameters were also estimated using Vegard's law assuming the lattice parameters of pure hematite as a = b = 5.038 Å and c = 13.772 Å.
- A comparison of the lattice parameters determined by refinement and Vegard's law are in good agreement.

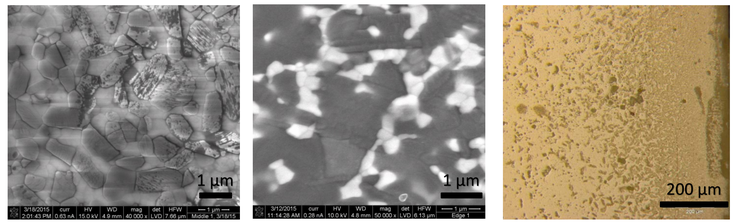


Refined histograms of α - Alumina/YSZ, b- Na-β”-alumina/YSZ, c- iron doped Alumina/YSZ before conversion and d- iron doped Alumina/YSZ after conversion

Comparison of lattice parameters determined by refinement and Vegard's Law indicate that hematite is completely dissolved in the alumina structure.

sample	Lattice parameter by XRD			by Vegard's law		
Lattice parameter of Alumina	a(Å)	b(Å)	c(Å)	a(Å)	b(Å)	c(Å)
α Alumina/YSZ before conversion	4.747	4.747	12.967	4.747	4.747	12.967
Iron doped α Alumina/YSZ before conversion	4.767	4.767	13.014	4.780	4.780	13.0519
Iron doped α Alumina/YSZ after conversion	4.758	4.758	13	4.780	4.780	13.0519

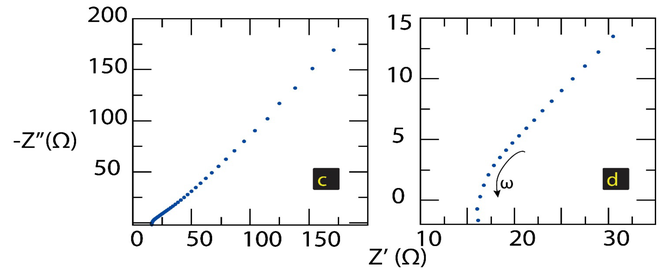
- as required for coupled transport to occur two phase composite in both unconverted and converted sample must be contiguous.
- the kinetics of conversion in the Fe-doped material is slower. This is determined by comparison of The conversion thickness in present work, 200 microns ,and the work by Parthasarathy and Virkar, 500 microns.



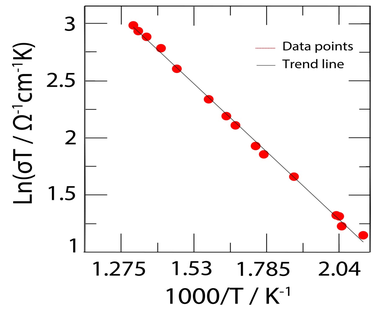
An SEM micrograph of Fe-doped α-Al_2O_3 + TZ-3Y, (b) An SEM image of the sample after conversion to Fe-doped Na-β”-alumina + TZ-3Y (c) An optical micrograph showing the boundary between the converted and the unconverted sample.

The estimated activation energy is 0.20 eV with a pre-exponential factor of 421 $\Omega^{-1}cm^{-1}K$. At 350ºC, the measured conductivity is 0.0163 Scm^{-1}. this conductivity is 30 times smaller than typical Na-β”-alumina conductivity results. The reason is attributed to (i) having a two phase mixture instead of one phase,(ii) lack of Li or Mg doping compared to typical Na-β”-alumina materials,(iii) inhomogeneity in mixture.

$$\sigma T = \sigma_0 \exp\left(\frac{-E_a}{K_B T}\right)$$



Electrochemical impedance spectra of the fully converted sample (c) at 290°C over the entire frequency range tested, (d) the high frequency regime at 290°C.



Arrhenius plot of the fully converted sample.

Conclusions

- The measurement confirmed the formation of Fe-doped Na-β”-alumina by the vapor phase process.
- The present work shows, it is possible to form two phase composites of doped Na-β”-alumina + TZ-3Y by the vapor phase process.
- Comparison of the conversion kinetics revealed a slower conversion compared to un-doped sample