

**MS10.13.07 PEROVSKITES FOR SOLID OXIDE FUEL CELLS.** Aniceta Skowron, Pengnian Huang and Anthony Petric, Department of Material Science and Engineering, McMaster University, Hamilton, Ontario, L8S 4L7 Canada

We have studied the structure and conductivity of perovskite-type  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ , the new, superior oxygen ion conductor (1, 2) for use as electrolyte in high temperature solid oxide fuel cells. Since the transport properties of substitutionally disordered and oxygen deficient materials are largely determined by their local structure, which may differ in symmetry from the average long range crystalline symmetry, we studied the local and average structures of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$  using powder neutron and electron diffraction and high resolution lattice imaging in TEM. Despite the macroscopic cubic symmetry revealed by neutron powder diffraction,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$  exhibits a lower symmetry short range order evidenced by, firstly, weak and sharp superstructure reflections and, secondly, streaks of diffuse scattering in the electron diffraction patterns. Neutron powder profile refinement shows that the oxygen nuclei are displaced from the sites of cubic symmetry in a manner similar to that in perovskite-related layered structure of brownmillerite. Thermal stability of the local structures was studied by high temperature electron diffraction and will be discussed in relation with the conductivity measurements. Modeling of the oxygen mobility was performed using the bond valence method (3).

#### References

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**MS10.13.08 STRUCTURE PROPERTY RELATIONS IN PYROCHLORE TYPE OXIDES FOR FUEL CELL APPLICATIONS.** Per Önnnerud, Kevin Eberman and Bernhardt J. Wuensch, Dept. of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge MA 02139

Pyrochlore oxides can exhibit high ionic conductivity or high electronic conductivity or both. They therefore have potential as Solid Oxide Fuel Cell (SOFC) materials. For the electrolyte materials of the SOFC a high ionic and a low electronic conductivity is a necessity while the cathodes require a mixed ionic and electronic conductivity. Service of the same structure in both functions would avoid materials compatibility problems.

The pyrochlore structure,  $\text{A}_2\text{B}_2\text{O}_7$ , is a superstructure of the fluorite type,  $(\text{A},\text{B})_4\text{O}_8$ , having twice the lattice parameter  $a=2a'$ , spacegroup  $\text{Fd}\bar{3}\text{m}$ . It was earlier suggested that the ratio  $r_{\text{A}}/r_{\text{B}}$  of the larger A cation and the smaller B cation is the governing parameter for the order in these systems. The pyrochlore structure can exhibit mainly two types of disorder: anti-site disorder of the cations and a Frenkel-like disorder on the oxygen-ion array. Neutron Rietveld analyses of the  $\text{Y}_2(\text{Zr}_y\text{Ti}_{1-y})_2\text{O}_7$  (YZT) system have shown that substitution of zirconium for the smaller titanium ion causes disordering of both the cation and anion arrays to a non-stoichiometric fluorite-type structure. As a consequence, the ionic conductivity increases. However, for a similar series of compounds,  $\text{Y}_2(\text{Sn}_y\text{Ti}_{1-y})_2\text{O}_7$ , with y's chosen to match the average radius of the B site in the YZT series, no disordering is observed. Although the cations partially disorder for the end member  $\text{Y}_2\text{Sn}_2\text{O}_7$ , no anion disorder is observed. A parameter very sensitive to the degree of disorder seems to be the positional coordinate ( $x \geq 0.375$ ) of the oxygen occupying the 48f position, which in a completely disordered structure becomes  $x=0.375$ .

The effect of the change in the state of disorder with composition has been used to interpret the variation in measurements of ionic conductivity obtained through impedance spectroscopy.

**PS10.13.09 SINGLE-CRYSTAL X-RAY DIFFRACTION STUDIES ON ELECTROCHEMICALLY LITHIATED  $\text{V}_6\text{O}_{13}$ .** Ö. Bergström, T. Gustafsson and J.O. Thomas, Inst. of Chem., Uppsala Univ., Box 531, S-751 21 Uppsala, Sweden

Much of today's battery technology research is driven by the need for new battery concepts for electric vehicle and portable electronics applications. The lithium-polymer battery (LPB) satisfies many of the requirements we can have of a modern battery, not least environmental acceptability. It contains a transition-metal oxide (TMO) as active electrochemical component.

In our efforts to understand lithium intercalation mechanisms in TMOs, we have earlier made in situ transmission XRD studies through an entire cell under electrochemical cycling [1]. A problem here has been to observe and distinguish the subtle structural effects of lithiation of the TMO particles from other cell-design features.

In this present work, we avoid this complication by constructing a LPB incorporating some single-crystals of  $\text{V}_6\text{O}_{13}$ . Resulting single-crystal XRD data indicates that previous published results from powder diffraction of lithiated  $\text{V}_6\text{O}_{13}$  must be re-evaluated.

This work has been supported earlier by ONR(USA), and currently by the EEC(Joule II), The Swedish Natural Science Research Council (NFR), and The Swedish Board for Technical Development (NUTEK).

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**PS10.13.10 NEUTRON POWDER DIFFRACTION OF OPERATING ELECTROCHEMICAL CELLS CONTAINING  $\text{LaNi}_{5-y}\text{Al}_y\text{D}_x$  ELECTRODES** G. L. Burr(IPNS), J. W. Richardson(IPNS), J. M. Carpenter(IPNS), W. Peng(CMT), L. Redey(CMT), A. N. Jansen(CMT), Argonne National Laboratory, Argonne, IL 60439, USA

Lanthanum-nickel hydride ( $\text{LaNi}_5\text{D}_x$ ) has been of interest as a battery material because of the ability of the intermetallic alloy to absorb large amounts of hydrogen (deuterium). It has been shown that substitution of some of the nickel with aluminum will increase the capacity of the electrode ten-fold. Rietveld profile refinements of neutron powder diffraction data on operating electrochemical cells have been performed to gain insight into the relationship between structural and electrochemical phenomena.

Our neutron powder diffraction studies on the aluminum substituted alloy indicate that aluminum preferentially substitutes into one available nickel site. Also, the addition of aluminum into the alloy leads to significant strain, as determined from the difference in peak broadening over that of the  $\text{LaNi}_5$  alloy.

The working cell consists of a rolled  $\text{LaNi}_{5-y}\text{Al}_y$  electrode with a  $\text{NiO}(\text{OD})$  counterelectrode, positioned outside of the neutron beam, in a  $\text{KOD}/\text{D}_2\text{O}$  electrolyte solution, all in a quartz tube. Contributions from the electrolyte and quartz tube are modeled by the Rietveld program.

Refinement of deuterium occupancy in a  $\text{LaNi}_{5-y}\text{Al}_y$  electrode indicates that the alpha phase (where x is small) in  $\text{LaNi}_{4.88}\text{Al}_{0.12}\text{D}_x$  can accept much more deuterium than the alpha phase for  $\text{LaNi}_5\text{D}_x$  ( $x = 1.2$  versus 0.5 for  $\text{LaNi}_5\text{D}_x$ ). No additional deuterium sites were identified. This is indicative of the aluminum contributing additional stability to deuterium in present sites. The Rietveld refinement was able to show that the deuteriums were preferentially loaded in sites near the aluminum.

A slow and steady decrease in the deuterium concentration (x) during a discharging cycle of a  $\text{LaNi}_{4.88}\text{Al}_{0.12}\text{D}_x$  cell was observed. Also cell volume in the same cycle also illustrated a similar decrease. The stress associated with the added aluminum is also present in the deuterated samples.

This presentation will focus on several  $\text{LaNi}_{5-y}\text{Al}_y$  alloys and how the structure effects the electrochemical loading of deuterium. The structural results observed in each step of the deuterium loading will also be presented.