

that a dynamic and flexible synthesis process leads to well-defined phase-pure and highly crystalline materials. Results from cathode materials containing chromium and iron substitution for manganese using diffraction and EXAFS are also reported. Questions regarding the possible clustering of Mn- or Cr-rich domains will be addressed.

MS10.13.03 RIETVELD REFINEMENTS OF α -MnO₂ AND LITHIATED α -MnO₂ FROM NEUTRON DATA. M. F. Mansuetto, D. W. Dees, C. S. Johnson, M. M. Thackeray, D. W. Vissers, D. Argyriou, ^aL. Christensen, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, ^a3M Corporation, 3M Center, Building 218-3CA-06, St. Paul, MN 55144

The structures of alpha manganese dioxide (α -MnO₂) and lithiated products have been refined from neutron data using the Rietveld method. α -MnO₂ was synthesized from alkaline battery grade γ -MnO₂ via a two step reaction scheme and dehydrated by heat-treatment. α -MnO₂ was chemically and electrochemically lithiated. Neutron diffraction data from powder samples were collected on the Special Environment Powder Diffractometer (SEPD) of the Intense Pulsed Neutron Source facility (IPNS) at Argonne National Laboratory. Rietveld refinements were carried out using GSAS (General Structure Analysis System). The refinements confirm that it is possible to synthesize an anhydrous α -MnO₂ framework structure without any stabilizing cation in the large (2 x 2) channels. Structural stability to electrochemical cycling when lithium is inserted into, and extracted from the α -MnO₂ framework will be discussed.

MS10.13.04 THE STRUCTURE OF THE LITHIUM ION INSERTION SPINEL Li_{1+x}Mn_{2-x}O₄. Helena Berg¹, Josh Thomas¹ & Erik Kelder². Institute of Chemistry, Uppsala University, Uppsala, Sweden¹. Dept. of Chemistry, Delft University of Technology, Delft, The Netherlands².

Various forms of the lithium insertion compound LiMn₂O₄ are currently being studied as potential cathode materials for lithium/polymer batteries. In this context, it is of the utmost interest to extend the capacity range of the material. This, in practice, means increasing the number of lithium ions which can be inserted and extracted reversibly from the material. One route has been to probe the possibility of preparing stoichiometric compounds with the general formulation Li_{1+x}Mn_{2-x}O₄ for 0 < x < 0.5, and thereafter examining their electrochemical properties. This is currently seen as a viable means of suppressing the cooperative Jahn-Teller distortion, which causes the spinel structure to pass through a cubic to tetragonal phase transition, with accompanying loss of lithium insertion capacity.

In this study, a neutron structure determination of a powder sample containing a two-phase mixture of the target compound Li_{1+x}Mn_{2-x}O₄ and another impurity phase Li₂MnO₃ have been studied. The two phases were refined simultaneously in a multiphase refinement mode, resulting in the effective formulation Li_{1.17}Mn_{1.83}O₄. This involves the occupation of an octahedral site hitherto not found to be occupied by lithium ions in any spinel, and is clearly related to the incidence of oxygen vacancies in the present structure. Unfortunately from a battery standpoint, the impurity phase, Li₂MnO₃, is not electrochemically active, and is therefore a troublesome source of capacity loss in any cell constructed using this mixture.

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MS10.13.05 DISORDERED CARBON FOR RECHARGEABLE LI-ION BATTERY. J. Simon Xue, J. R. Dahn*, W. Xing*, Ultralife Batteries, Inc., Newark, N.Y. 14513, U.S.A. *Department of Physics, Simon Fraser University, Burnaby, B.C., Canada V5A 1S6.

Disordered carbonaceous anode materials for Li-ion batteries can be made using two different types of inexpensive precursors: petroleum products (such as phenolic, epoxy resins) or natural carbohydrates (sugar, starch, or cellulose). These carbons usually have a disordered structure composed of randomly stacked graphene sheets. Many of these samples show evidence for a substantial number of nanoscopic pores about 5 to 10 angstroms in radius.

Lithium insertion mechanism in these materials has been discussed previously¹. Some of those pyrolyzed carbohydrates have reversible specific capacities as high as 640 mAh/g, irreversible capacities of 140 mAh/g and show little hysteresis. Their electrochemical behavior appears similar to that of "pseudoisotropic carbon", developed by researchers at Kureha². The materials are advantageous over the graphitic anode in the following aspects: 1) low cost, 2) simplicity in processing, and 3) high capacity. The synthesis, structure and electrochemical testing results will be presented.

1. J. R. Dahn, et al., Science, 270(1995)590.

2. N. Sonobe, et al., Paper 2B09, in Extended Abstracts, p.47, of 35th Battery Symposium in Japan, Nov. (1994) Nagoya, Japan.

MS10.13.06 MATERIALS DESIGN OF LITHIUM IONIC CONDUCTOR WITH THE SPINEL STRUCTURE. Ryoji Kanno, Department of Chemistry, Faculty of Science, Kobe University, Kobe 657 Japan

Materials, so-called "ionic conductors" or "solid electrolytes", show high ionic diffusion in solids and are promising electrolyte systems for future lithium batteries. Materials design of the ionic conductors was initially based on the classical ionic conductor, alpha-AgI; high ionic conductivity at room-temperature has been obtained for silver and copper electrolytes. However, lithium ionic conductivity is still low at room-temperature and it is still necessary to search for new lithium system. Ionic conductors usually show a transformation from low to high ionic conduction state. By considering the phenomena, we might have an idea for designing new materials with high ionic conductivity. In the present paper, materials syntheses and the transformation from low to high ionic conduction states are discussed for lithium halide spinels, oxide spinels, and other materials based on a cubic close packed anion array.

The close packed anion array may be considered as a framework structure in which mobile species can diffuse. The halide spinels, Li₂MX₄ (M=transition metal), oxide spinels, LiM₂O₄, and other layered rocksalt-type oxides, LiMO₂ may have similar diffusion pathways. Among these, the halide system is more suitable for high lithium ionic diffusion because of the larger ionic radii and larger polarizabilities of anions. High-temperature behavior of these materials is studied using conductivity measurements, and X-ray and neutron diffraction methods.

The halide spinels show a gradual slope change in the Arrhenius conductivity plots which corresponds to a transition from low to high ionic conducting state. The lithium ions have gradually left their normal site to the interstitial site, which may be common phenomena for famous high ionic conductors such as PbF₂ or Rb₄Cu₁₆I₇Cl₁₃. Further, the transition to high ionic conducting states are discussed in comparison with other materials showing first order phase transition.