PS10.12.17 INTERSTITIAL TRANSITION METAL ORDERING IN WIDE RANGE NON-STOICHIOMETRIC $M_{2+x}Sn_2$ (M=Co,Ni) SOLID SOLUTIONS.

R.L. Withers and A-K.Larsson, Research School of Chemistry, Australian National University, Canberra, ACT, 0200 Australia

An electron diffraction study of "disordered" γ-$Co_{2+x}Sn_2$ (0.76<x<1.26) and γ-$Ni_{2+x}Sn_2$ (0.70<x<1.19) has revealed the presence of a spectacular, sharp and highly structured diffuse intensity distribution to which the low temperature ordered γ' superstructures are clearly closely related. The underlying M_2Sn_2 average structure is of *NiAs* type (space group symmetry $P6_3/mmc$, a ≈ 4.1 Å, c ≈ 5.2 Å) with additional interstitial transition metal atoms occupying trigonal bipyramidal sites in the Sn sub-lattice. The ordering of these interstitial transition metal atoms and the associated structural relaxation gives rise to the observed diffuse distribution.

The basic shape of the diffuse distribution appears to be based upon intertwined, undulating, approximately cylindrical channels of diffuse intensity running along the **c*** directions of reciprocal space. The intensity observed when rotating around **c***, however, depends strongly upon azimuthal angle. The general topology of the diffuse distribution does not change significantly with composition across the solid solution field, but the amplitude of the undulating channels does: this amplitude is shown to be directly proportional to composition. The strongest satellite reflections characteristic of the low temperature ordered γ'-phases fall directly onto the diffuse distribution of the γ-phase while the characteristic extinction conditions of the ordered γ'-phases are mirrored in the diffuse distribution of the γ-phase.

A modulation wave approach is used to deduce the implications of the observed diffuse distribution for local interstitial transition metal ordering. Minimization of macroscopic strain along close packed <110> directions is shown to be responsible for the characteristic absence of diffuse intensity in {h,-h,l}* reciprocal lattice planes.

PS10.12.18 POINT DEFECT CLUSTERS IN PbTe:In.

A.K. Tkalich[a], K.D. Chtcherbatcheva[a] and V.P. Zlomanov[b]. [a]Moscow Institute of Steel and Alloys, Moscow, Russia; [b]Moscow State University, Moscow, Russia

The asymptotic X-ray diffuse scattering (AXRDS) has been used to characterize the point defect structure in $Pb_{1-x}In_xTe$ (x=0.01) single crystals doped above the point of hole compensation x~0.004. From the AXRDS intensity profile (Fig.1) taken along the diffraction vector near to (400) reciprocal lattice point on a triple-crystal diffractometer, it is evident that there are microdefects (the submicron point defects clusters) of both vacancionic (at q<0) and interstitial (at q>0) type. Herewith, the concentration of the former is greater than that of the latter. The typical size of microdefects is approximately of ~0.01-0.1 μm. The interstitial microdefects are supposedly formed from the Te interstitials created during the post-crystallization cooling cycle due to the decomposition of solid solution enriched with Te, while the vacancionic microdefects should contain the In impurity atoms and vacancies of lead.

The role of the In impurity and native point defects in the effect of Fermi level pinning is discussed taking into account our recent photoemission data on In states in PbTe.

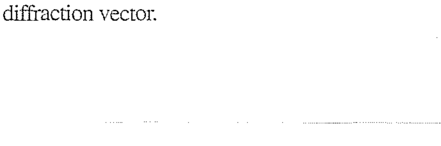


Fig.1 (400) AXRDS intensity profile in PbTe:In. I - intensity, q - deviation from the diffraction vector.

Materials XIII
Advanced Battery and Fuel Cell Materials

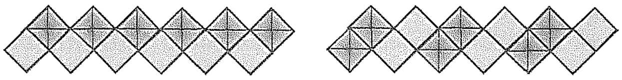
MS10.13.01 CRYSTAL CHEMISTRY OF LAYERED VANADIUM OXIDE CATHODE MATERIALS.

Peter Y. Zavalij, M. Stanley Whittingham. State University of New York at Binghamton, Binghamton, NY 13902-6016, USA

Structural analysis of V_2O_5 layers as well as VO_3 and V_3O_8 polyanions has been done based on known structures with square pyramidal coordination of vanadium and stoichiometry V_2O_5, $M_xV_2O_5$, M_xVO_3, $M_xV_3O_8$, $M_xV_6O_{15}$, etc. including our new compounds ($LiV_2O_4 \cdot H_2O$, $TMAV_4O_{10}$, $TMAV_2O_5$ and $DTAV_3O_8$, where TMA = tetramethyl ammonium, DTA = dodecyl trimethyl ammonium) with novel topography of layers.

The unique layered structures of vanadium oxides and their derivatives are of particular interest because of their capacity to intercalate lithium and other cations between their layers that makes them promising candidates for cathode materials in secondary lithium batteries.

The most common V-polyhedron is a square pyramid VO_5 with double bonded oxygen in its vertex. Those polyhedra when sharing edges form double chain with stoichiometry VO_3 which exist by itself in $KVO_3 \cdot H_2O$ and $Co(VO_3)_2 \cdot 4H_2O$. The topography of the double chains can be simply presented by symbolic formula using two symbols (U - up and D - down) which show the orientation of the square pyramid. The symmetry of the formula by using simple rules leads to 10 possible symmetry groups of the double chains. In most cases those double chains form layers by sharing single bonded oxygen atoms of basis. Using different ways of joining chains to the layers the possible symmetry, topography, and dimensions of V_2O_5 layers has been developed. Those conclusions are used to predict the structure of the layers in the novel compounds. The structure of V_2O_5 layers is also discussed from the point of view of their capacity to easily accept additional charges that yields rich intercalation opportunities in contrary to frameworks constructed with VO_4 tetrahedra.



MS10.13.02 STRUCTURAL ASPECTS OF TRANSITION METAL OXIDE CATHODE MATERIALS FOR LITHIUM BATTERIES.

Christina Lampe-Önnerud, Massachusetts Institute of Technology, Cambridge MA 02139, S. Greenbaum, P.E. Stallworth, S. Kostov, and M. denBoer, The City University of New York, Hunter College, New York NY 10021, Denis Fauteux and Arthur Massucco, Arthur D. Little Inc., Battery Technology Center, Cambridge MA 02140

First-row transition metal oxides have over the years received much interest as cathode materials for lithium intercalation in rechargeable cells. Strong candidates for a future thin-film battery include $Li_xV_6O_{13}$, $LiCoO_2$, and spinel $Li_xMn_2O_4$ systems, exhibiting high capacity in an attractive voltage range for application devices. The crystallinity and atomic arrangement will be addressed in the light of X-ray and neutron diffraction in combination with spectroscopic evaluation by NEXAFS, EPR and NMR.

Neutron diffraction shows that as lithium is intercalated into V_60_{13}, the (0,0,0)position starts to fill. However, upon further intercalation, powder diffraction identifies an increasing amorphous component. ^{51}V and ^7Li NMR line shape and spin-lattice relaxation time measurements for $Li_xV_6O_{13}$ (0<x<6) shows some changes in conduction pathways or mechanisms as a function of x, although the NMR results are dominated by the presence of paramagnetic V^{4+}. Our previous findings identifying four phases ($Li_xV_6O_{13}$; x=0.5, 1.5, 3, and 6) were confirmed by the spectroscopic measurements.

X-ray Rietveld refinements on $LiCoO_2$ and spinel $Li_xMn_2O_4$ show 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-MnO_2 AND LITHIATED α-MnO_2 FROM NEUTRON DATA.

M. F. Mansuetto, D. W. Dees, C. S. Johnson, M. M. Thackeray, D. W. Vissers, D. Argyriou, [a]L. Christensen, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, [a]3M Corporation, 3M Center, Building 218-3CA-06, St. Paul, MN 55144

The structures of alpha manganese dioxide (α-MnO_2) and lithiated products have been refined from neutron data using the Rietveld method. α-MnO_2 was synthesized from alkaline battery grade γ-MnO_2 via a two step reaction scheme and dehydrated by heat-treatment. α-MnO_2 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-MnO_2 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-MnO_2 framework will be discussed.

MS10.13.04 THE STRUCTURE OF THE LITHIUM ION INSERTION SPINEL $Li_{1+x}Mn_{2-x}O_4$.

Helena Berg[1], Josh Thomas[1] & Erik Kelder[2], Institute of Chemistry, Uppsala University, Uppsala, Sweden[1]. Dept. of Chemistry, Delft University of Technology, Delft, The Netherlands[2].

Various forms of the lithium insertion compound $LiMn_2O_4$ 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 $Li_{1+x}Mn_{2-x}O_4$ 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 neuton structure determination of a powder sample containing a two-phase mixture of the target compound $Li_{1+x}Mn_{2-x}O_4$ and another impurity phase Li_2MnO_3 have been studied. The two phases were refined simultaniously in a multiphase refinement mode, resulting in the effective formulation $Li_{1.17}Mn_{1.83}O_4$. This involves the occupation of an octahedral site hithero 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, Li_2MnO_3, 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 previously[1]. 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 Kureha[2]. 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, Li_2MX_4 (M=transition metal), oxide spinels, LiM_2O_4, and other layered rocksalt-type oxides, $LiMO_2$ 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 PbF_2 or $Rb_4Cu_{16}I_7Cl_{13}$. Further, the transition to high ionic conducting states are discussed in comparison with other materials showing first order phase transition.