

a transformation from  $Pn$  to  $Pmn2_1$ , confirmed by XRD. The enthalpy change was estimated at  $4.7 \pm 0.2$  kJ/mol, which agrees reasonably well with total-energy difference of 4.1 kJ/mol from GGA+U calculations.

The stability of de-lithiated  $MnSiO_4$  structures resulting from  $Li_2MnSiO_4$   $Pn$  and  $Pmn2_1$  polymorphs was compared by computing *ab initio* elastic coefficients using VASP GGA+U potentials. Results indicated that  $MnSiO_4$  arising from them are both soft materials, but their calculated 3D plots of anisotropic tensile modulus or small-shear modulus did not indicate a spontaneous transition to another phase, suggesting stability of both  $Pn$  and  $Pmn2_1$   $MnSiO_4$  against possible second-order phase transitions that preserve cell translations. The  $Pmn2_1$  polymorph is known to be unstable with respect to  $C2/m$   $MnSiO_4$ , but this first-order transformation would require a rearrangement of atomic bonds, which may or may not happen spontaneously.

Finally, the electrochemical performance of the new polymorphs was assessed and compared to  $Pmn2_1$   $Li_2MnSiO_4$ . Most of the electrochemical data on  $Li_2MnSiO_4$  reported in the literature is on the latter polymorph. Here, polymorph-specific features are identified by cyclic voltammetry and galvanostatic cycling.

**Keywords:** Lithium-ion battery, DFT calculations, Silicates

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#### Li<sup>+</sup> Ion diffusion and vacancy formation in the $Li_{1-x}FeO_2$ electrode material

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The ‘corrugated layer’  $Pmnm$  phase of  $LiFeO_2$  ( $a=4.061$ ,  $b=2.962$ ,  $c=6.032$  Å) is an attractive electrode material for reversible lithium ion batteries, because inexpensive and not toxic [1,2]. The distorted rocksalt superstructure contains alternate Li-O and Fe-O double layers, corresponding to (011) rocksalt planes. We recently proposed a satisfactory interpretation of the complex electrochemical reactions occurring in a  $Pmnm$ - $LiFeO_2$  cathode, on the basis of first-principles calculations of the corresponding voltages and comparison with data from experimental charge/discharge curves [3]. Here models for Li<sup>+</sup> ion mobility pathways in the (001) lithium layers of stoichiometric and defective  $Li_{1-x}FeO_2$  are presented and discussed.

The ground-state crystal energy was computed by DFT (Density-Functional-Theory) methods, based on use of the hybrid B3LYP functional with localized Gaussian-type basis sets [4]. Appropriate supercells were devised as needed, with full least-energy structure optimization. In the defect-free case ( $x=0$ ), ion diffusion was found to take place cooperatively inside a fraction of ‘active’ lithium layers, separated by inert ones. This condition is necessary to avoid excessive strain of the crystal structure. The mobility pathway based on a Li bottleneck state in tetrahedral coordination is slightly preferred over that implying an intermediate state with linearly coordinated Li, according to a predicted  $\Delta E_a$  activation barrier of 0.410 vs. 0.468 eV. The ion diffusivity  $D$ , with jump distance of 3 Å, was then calculated in the range between  $1.9 \times 10^{-10}$  and  $1.8 \times 10^{-11}$  cm<sup>2</sup> s<sup>-1</sup> at 300 K. This corresponds to the behaviour of a satisfactory ion conductor.

For the  $Li_{0.75}FeO_2$  deintercalated material a number of low energy vacancy configurations were considered, investigating also the vacancy influence on electron density of states and atomic charge distribution. The most favourable structural arrangements have a vacancy formation energy  $E_f$  in the 4.3 to 4.5 eV range. One of them,  $P2_1/m$ - $Li_{0.75}FeO_2$ , was found to favour an ion hopping pathway based on the linear-type bottleneck state, with a quite low activation barrier of 0.30 eV; further, in this case no inert layers are required to limit the structural strain. A significantly improved ion conductivity thus ensues, with respect

to stoichiometric  $LiFeO_2$ . Accordingly, in the defective material the predicted ionic conductivity at room temperature rises from  $10^{-5} \div 10^{-6}$  ( $LiFeO_2$ ) to  $4 \times 10^{-4}$  ohm<sup>-1</sup>cm<sup>-1</sup> ( $Li_{0.75}FeO_2$ ). The present results show that, by developing reliable low-energy structural models for the vacancy arrangements in Li-deintercalated phases, it is possible to successfully determine ion mobility pathways and to predict conductivity values in such electrode materials.

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**Keywords:** first-principles calculations, ion diffusion, lithium material

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#### Structure and Thermoelectric Properties of Ca-M-Co-O (M=Sr, Zn, and La)

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Thermoelectric research is of increasing importance in the development of technologies for improving vehicular fuel economy and for mitigating green house gas emissions. There is a well-defined need for efficient energy conversion materials and environmentally friendly technologies over the next twenty years. For waste heat energy conversion applications, oxide materials which have high temperature stability are potential candidates. In the Ca-M-Co-O (M=Sr, Zn, and La) systems, in addition to the well-known  $Ca_3Co_4O_9$  phase (with misfit layered structure) that exhibits excellent thermoelectric property, other interesting phases include members of the homologous series,  $A_{n+2}Co_nCo'O_{3n+3}$  (where A= Sr, Ca, (Ca,Sr) or (Sr,Ca)), which consist of 1-dimensional parallel  $Co_2O_6^{6-}$  chains. While the members of the  $A_{n+2}Co_nCo'O_{3n+3}$  series have reasonably high Seebeck coefficients and relatively low thermal conductivity, the electrical conductivity needs to be increased in order to achieve higher  $ZT$  (figure of merit) values. This paper discusses our phase equilibria/structural/property studies of selected cobaltites, including those in the  $SrO$ - $CaO$ - $CoO_x$ ,  $CaO$ - $ZnO$ - $CoO_x$ , and  $CaO$ - $La_2O_3$ - $CoO_x$  systems.

**Keywords:** thermoelectric, phase-equilibria, structure

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#### Structural Changes and Voltage Output in Defect Perovskite Cathode Materials

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The development of new high capacity cathodes is becoming increasingly important as currently used materials reach their critical