Lithium cobalt phosphate: a high voltage lithium ion cathode material

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In recent years, lithium-conducting phosphates, a new class of cathode materials for lithium ion batteries, has attracted great attention. The iron phosphate in particular has been the focus of several research groups. This is because this material is environmentally friendly, thermally stable and shows very good electrochemical performance. The strong covalent bonding between the oxygen and P^{5+} to form $(PO_4)^{3-}$ units allows for greater stabilization of the structure compared to layered oxides, e.g. $LiCoO_2$ where the oxide layers are more weakly bound, Fig. 1. This strong covalency stabilizes the anti-bonding Fe^{3+}/Fe^{2+} state through an Fe-O-P inductive effect.

Lithium conducting phosphates with the olivine structure $LiMPO_4$ (M = Fe, Mn, Co, Ni and etc.) have a theoretical capacity of 170 $mAhg^{-1}$, higher than that of lithium cobalt oxide (practical specific capacity). Among these olivine phosphates, cobalt phosphate has the highest energy density because its redox potential is 4.8V vs. (Li/Li^+). However, $LiCoPO_4$ has been reported to have a specific capacities less than 100$mAhg^{-1}$ even at rates as low as C/10.[2] To our knowledge, no work about this material with respect to its cycling performance, such as cycle life and rate capability, has been reported. Here we report on the performance of $LiCoPO_4$ improved through doping with other elements. The electrochemical voltage profile, Fig 2 shows a dramatic reduction of the over-potential upon doping. The doped $LiCoPO_4$ can yield 135 $mAhg^{-1}$ of discharge capacity at C/20 and 125 $mAhg^{-1}$ at C/5.

Using this optimized cathode material, rocking chair batteries with MCMB as anode materials were made, and cycled at C/2, see Figs 3-4. The loading of active material on cathode was 20$mgcm^{-2}$, and the initial capacity was 118$mAhg^{-1}$ at C/2. More data will be presented, as including thermal stability and rate capability. In spite of the high voltage lithium cobalt phosphate can be optimized to be a very promising high voltage cathode material for lithium ion batteries.

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References

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[2] K. Amine, H. Asuda and M. Yamach*i* *Electrochem. Soc. St. Lett*, 3(4) 178 (2000)

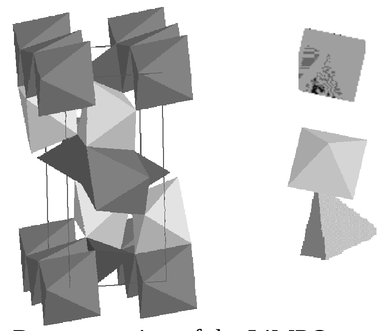

Fig. 1: Representation of the $LiMPO_4$ structure.

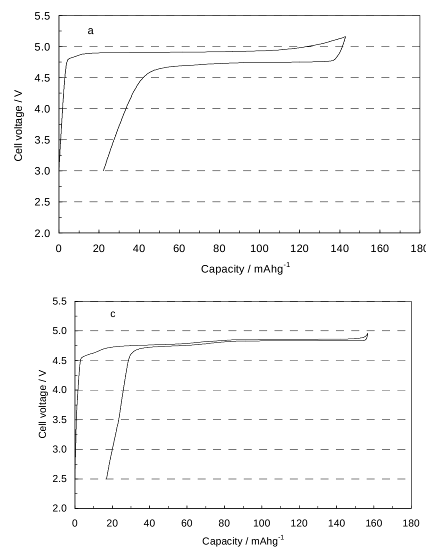

Fig 2. EVS for $LiCoPO_4$ (a), doped A sample (b) and doped B sample (c).

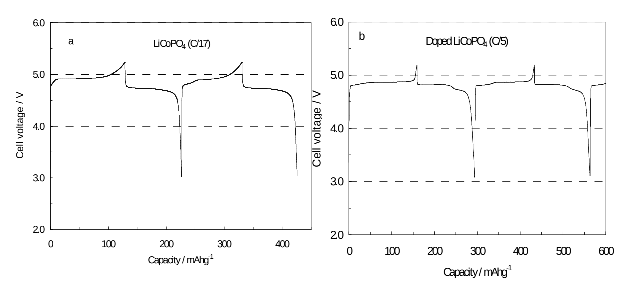

Fig 3. Charge and discharge curves of Li cells : (a) $LiCoPO_4$ (C/17) and (b) doped $LiCoPO_4$ (C/5).

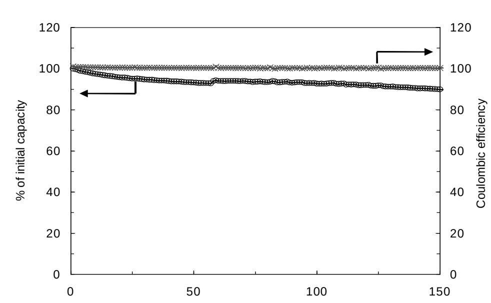

Fig 4. Capacity retention of doped $LiCoPO_4$/MCMB cell on cycling (C/2).

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