

Novel Cathode Materials for Rechargeable Batteries

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Abstract: *Lithium batteries have made substantial and significant gains in the last three decades for the dominant rechargeable battery for consumer portable applications. The cost, safety, environmental friendliness and long operational life of the electrode materials are of major concern for the application of large scale powerful and energy storage lithium ion batteries. Almost all of the research and commercialization of cathode materials has centered on two classes of materials. The first contains layered compounds with an anion close packed or almost close packed lattice and the materials in the second group have more open structures. LiCoO_2 has the $\alpha\text{-NaFeO}_2$ structure with the oxygens in a cubic close packed arrangement. On complete removal of the lithium, the oxygen layers rearrange themselves to give hexagonal close packing of the oxygen in CoO_2 . Compounds with low lithium contents appear to be unstable due to the high effective equilibrium oxygen partial pressure, so that such cells are inherently unstable and therefore dangerous in contact with organic solvents. Comparing to the commercial LiCoO_2 , LiNiO_2 , LiMn_2O_4 and their derivatives, LiFePO_4 cathode material almost has the same outstanding advantages of abundant available resource and low cost, excellent thermal stability, excellent cycling performance, satisfactory safety, environmentally benign and low toxicity. LiFePO_4 is the first cathode material with potentially low cost and plentiful elements and also environmentally benign that could have a major impact in electrochemical energy storage. Nanostructured electrodes have attracted a great deal of scientific and technical interest as a result of their unique physical and chemical properties. It can be anticipated that totally new materials with unexpected properties will be discovered, so that the goal of cycling per transition metal at still higher rates.*

Keywords: Cathode Materials, Structure, Capacity, Electrochemical and Environmental Stability.

1. Introduction

The lithium battery industry is undergoing rapid expansion, now representing the largest segment of the portable battery industry and dominating the computer, cell phone and camera power source industry. Higher performance active materials containing cathodes have been strongly required for the achievement of advanced lithium-ion rechargeable batteries. A battery is a transducer that converts chemical energy into electrical energy and vice versa. It contains an anode, a cathode and an electrolyte. The anode, in the case of a lithium battery, is the source of lithium ions. The cathode is the sink for the lithium ions. The electrolyte provides for the separation of ionic transport and electronic transport. Though the ions flow through the electrolyte, the anode and cathode must be physically separated to prevent an electrical short. This is accomplished by using a porous separator material, which allows wetting by the electrolyte and the flow of lithium ions through it. The key requirements for a material to be successfully used as a cathode in a rechargeable lithium battery are: the material contains a readily reducible/oxidizable ion, the material reacts with lithium in a reversible manner, the material reacts with lithium with a high free energy of reaction, the material reacts with lithium very rapidly both on insertion and removal, the material is a good electronic conductor, preferably a metal and the material is stable, i.e., not change structure or otherwise degrade, to over discharge and overcharge, the material is low cost and the material is environmentally benign. Almost all of the research and commercialization of cathode materials has centered on two classes of materials. The first contains layered compounds with an anion close packed or almost close packed lattice and the materials in the second group have more open structures. Many primary lithium batteries have been developed for use in the medical field starting with the lithium iodine cell. Future medical devices,

such as heart assist devices, will require rechargeable systems because the capacity of primary cells cannot provide the power needed for active medical devices.

2. Cathode Materials

Good enough recognized that LiCoO_2 had a structure similar to the layered structures of the dichalcogenides and showed that the lithium could be removed electrochemically, thus making it a viable cathode material. This material is mainly used as a major cathode material in commercial Lithium ion batteries as a result of its excellent electrochemical properties and high electrode density. Recently, nanostructured electrodes have attracted a great deal of scientific and technical interest as a result of their unique physical and chemical properties that bulk materials may not possess. Because of their large surface area to volume ratio, the nanoparticles can be used in electrochemical energy storage devices to provide both high power and high energy density. Although Lithium ion batteries are attractive power-storage devices that have high energy density, their high power density is generally low due to the high level of polarization at higher current rates. LiCoO_2 has the $\alpha\text{-NaFeO}_2$ structure with the oxygens in a cubic close packed arrangement. On complete removal of the lithium, the oxygen layers rearrange themselves to give hexagonal close packing of the oxygen in CoO_2 . Although the LiCoO_2 cathode dominates the rechargeable lithium battery market, there is a limited availability of cobalt, which causes it to have a high price. This price limits its use to small cells, such as those used in computers, cell phones and cameras. An alternative cathode will be needed for large-scale applications, as envisioned in high energy voltage or for load leveling [1]. The LiCoO_2 patent covered more than this one cathode, describing all layered transition metal oxides with the $\alpha\text{-NaFeO}_2$ structure where the transition metal is vanadium through nickel.

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Lithium nickel oxide, LiNiO_2 , is isostructural with lithium cobalt oxide but has not been pursued in the pure state as a battery cathode for a variety of reasons, even though nickel is more readily available than cobalt. It is not clear that stoichiometric LiNiO_2 exists. The stability of Li intercalation compounds is largely affected by accompanying phase transformations during intercalation and deintercalation of Li ions. The structural transformations usually cause nonuniform distortion of the crystal lattice structure. Since metal oxides with low ductility initiate mechanically induced microcracks resulting from lattice strain, the reversibility of Li intercalation sharply deteriorates. Among the 4 V cathode materials, LiNiO_2 has the highest degree of lithium intercalation capability. However, it exhibits severe phase transformations over $0 < x \leq 0.8$ in $\text{Li}_{1-x}\text{NiO}_2$. It is evident that excess nickel as in $\text{Li}_{1-y}\text{Ni}_{1+y}\text{O}_2$; thus, nickel is always found in the lithium layer, which pins the NiO_2 layers together, thereby reducing the lithium diffusion coefficient and the power capability of the electrode [2]. Compounds with low lithium contents appear to be unstable due to the high effective equilibrium oxygen partial pressure, so that such cells are inherently unstable and therefore dangerous in contact with organic solvents. Unlike cobalt and nickel, manganese does not form a stable LiMnO_2 phase with the LiCoO_2 structure, with the spinel structure being the stable phase at the composition $\text{Li}_{1.5}\text{MnO}_2$. As there are a myriad of structures with the 1:2 Mn:O ratio, other structures may be stable at different lithium contents.

In spinel cathode LiMn_2O_4 , the anion lattice contains cubic close-packed oxygen ions and is closely related to the $\alpha\text{-NaFeO}_2$ layer structure, differing only in the distribution of the cations among the available octahedral and tetrahedral sites. The discharge proceeds in predominantly two steps, one around 4 V and the other around 3 V [3]. Usually only the 4 V plateau is used, so that the cell is constructed in the discharged state and must be charged before use just as for LiCoO_2 . It is evident that the value of the cubic lattice parameter, which is directly related to the average oxidation state of the manganese, is critical to obtain effective cycling. The lattice parameter should preferably be 8.23 Å or less and such values are associated with lithium rich materials, $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$, where the average manganese oxidation state is 3.58 or higher; this value minimizes dissolution of manganese and also the impact of the Jahn-Teller distortion associated with the Mn^{3+} ion. This spinel is presently the center of much interest as the cathode of a high power lithium battery for hybrid electric vehicles, even though under high drain rates its capacity is only 80 mA/g. Over past years, extensive effort has been made to enhance the mixed conductivity of electrode materials by admixing high conductive carbon based materials as conducting networks. Recently, Graphene, a monolayer of carbon atoms, shows superior electrical conductivity, high surface area and good mechanical flexibility. The characteristics provide a highly conductive matrix and offer a high contact area between electrolyte and electrode, facilitating transportation of Li and electrons into the electrode. Thus, incorporating the nanoparticles with the graphene matrix can be an ideal strategy to improve specific capacity and cycling stability.

Substituted nickel oxides, such as $\text{LiNi}_{1-y-z}\text{O}_y\text{Al}_z\text{O}_2$, are prime candidates for the cathode of advanced lithium batteries for use in large scale systems as required for hybrid electric vehicles. Work on these cobalt substituted $\alpha\text{-NaFeO}_2$ structure materials, where manganese is the redox-active ion, has essentially ceased because of the inability to maintain the structure relative to conversion to the spinel structure under realistic cycling conditions. Doping elements other than cobalt have also been investigated, but substitution by nickel leads to a system where the manganese becomes the structure stabilizer and nickel the electrochemically active ion. These compounds are thus best described as substituted nickel oxides in which the manganese remains in the tetravalent state and the nickel is redox active between the +2 and +4 oxidation states; the manganese helps in reducing the cost and stabilizing the lattice. Cobalt, as will be discussed below, plays a critical role in controlling the ordering of the 3d ions in the structure. The electrochemically active element in this compound is nickel, which cycles between the +2 and +4 valence states, while the manganese remains as +4 throughout independent of the lithium content. First principal quantum mechanical calculations as well as structural measurements confirm this redox assignment. As the manganese is always 4+, there is no concern with the Jahn-Teller distortion associated with the Mn^{3+} ion. About one half of the lithium could be removed in an electrochemical cell, with only about one half of that being reintercalated on discharge; this is believed to be due to cation, probably titanium, migration into the lithium layer.

LiFePO_4 , is the first cathode material with potentially low cost and plentiful elements and also environmentally benign that could have a major impact in electrochemical energy storage. For LiFePO_4 , the discharge potential is about 3.4 V vs lithium and no obvious capacity fading was observed even after several hundred cycles. Its capacity approaches 170 Ah/kg, higher than that obtained by LiCoO_2 and comparable to stabilized LiNiO_2 , and moreover, it is very stable during discharge/recharge [4]. LiFePO_4 can be synthesized by high temperature reactions, under hydrothermal conditions, or by sol gel methods. Although the olivine phase can be very easily synthesized hydrothermally within just a few minutes and its X-ray pattern looks good, it gives poor electrochemical properties; a close examination of the structure revealed that there are about 7% iron atoms in the lithium site and this is reflected in the lattice parameters. These iron atoms essentially block diffusion of the lithium ions, as the diffusion is fast only along the tunnel and not between them; thus, it will be critical in the use of this material to ensure ordering of the lithium and iron atoms. It is essential to understand the long-term stability of electrode materials to ensure the extended life of any battery. Thus, it is important to better understand the reactivity of both the LiFePO_4 and the FePO_4 orthorhombic phases. An electrochemical study where the LiFePO_4 cathode was subjected to a discharge down to 1.0 V at 0.4 mA/cm² confirmed that lithium reacts with destruction of the LiFePO_4 lattice and considerable loss of capacity. After five cycles the capacity had dropped by 80%. Thus, lithium iron phosphate cells will require over discharge protection in commercial applications. On the other hand, no evidence has been found

for the conversion of the metastable orthorhombic FePO_4 phase to the quartz like trigonal phase under normal electrochemical conditions.

3. Conclusion

Lithium ion batteries are widely used in portable equipment, such as mobile phone, notebook computer, electron instrument, and so on. But in high power and high energy field, lithium ion batteries are rarely used, such as electric vehicles, hybrid electric vehicles, dispersed energy storage systems and space batteries. The cost, safety, environmental friendliness and long operational life of the electrode materials are of major concern for the application of large scale powerful and energy storage lithium ion batteries. However, the next future opportunities will be much tougher to conquer as they mostly demand higher power capabilities at lower costs and often in larger systems with enhanced safety. The layered oxides will continue their ongoing improvement with mixed transition metals slowly displacing the pure cobalt system. The stability of Li intercalation compounds is largely affected by accompanying phase transformations during intercalation and deintercalation of Lithium ions. LiCoO_2 has the $\alpha\text{-NaFeO}_2$ structure with the oxygens in a cubic close packed arrangement. Cobalt dissolution, structural changes and oxidative de-composition of the electrolyte produce a dramatic increase in the capacity fade at the higher potentials. It can be anticipated that totally new materials with unexpected properties will be discovered, so that the goal of cycling per transition metal at still higher rates.

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