CHAPTER II

LITERATURE REVIEW

2.1 Lithium Ion Battery (Li-ion battery)

The need of power sources with a high energy, light weight and environmental safety limits the use of poisonous Pb and Cd batteries. Li-ion battery is an interesting power source for nowadays living since the safety problems and also the cycle life —presences Li-dendrites — have been solved. Li-ion battery has many advantages over the traditional rechargeable battery like lead acid and Ni-Cd, for example, a high energy density, high average output voltage (3.6-3.7 V), low self discharge (<5% per month), no memory effect, high cycling behavior (>1200), high rate capability, high coulomb efficiency (~ 100% in the first time cycle), wide work temperature range (-25 to 45 °C up to be 70 °C), and environmental safety. It can be called "a green battery". Li-ion battery has been developed very rapidly, and widely applied in light electronics, e.g., portable telephone, computer and digital camera etc. *(Nishi Y. 1997, Besenhard JO. 1999 and Wu YP. et al., 2002).*

Due to the evident advantages of Li-ion battery, the researches on electrode materials are still active. There are many preparation methods that have been explored, including incorporation of heteroatom *(Wu YP. et al., 2002)*, composite technology *(Wu YP. et al., 2003)*, soft-chemistry method, such as ion exchange, hydrothermal and oxidation-reduction reactions *(Manthiram A. et al., 1999)*, mechano-chemical method *(Ning LJ. et al., 2004)*, template methods, arc discharge with carbon bars, pulsed laser deposition, plasma-enhanced chemical vapor deposition, radio-frequency magnetron sputtering *(Wu YP. et al., 2003)*, and sol-gel methods *(Livage J. et al., 1989, Nishi Y. 1997, Besenhard JO. 1999 and Wu YP. et al., 2002).*

2.2 Electrode Materials for Li-ion Battery

Since 1990, the electrode materials for Li-ion battery have become very active. It is necessary to use the electrode materials, having very specific structures

and properties. For the positive electrode materials, they are mainly including lithium cobalt oxide (LiCoO$_2$) using metal oxide, having Li intercalation capability *(Linden (Ed.), et al., 1995)*. LiCoO$_2$ is not as stable as other potential electrode materials and can undergo degradation or failure when overcharged *(Belov et al., 2008 and C.-H. Doh et al., 2008)*. It can degrade during cycling. Reasons are following; cobalt is dissolved in the electrolyte when the electrode is delithiated during charging *(Amatucci et al., 1996)*, making less lithium be able to intercalate during discharge, and the CoO$_2$ layer formed after full delithiation shears from the electrode surface *(Amatucci et al., 1996)*, which also results in less capacity for lithium intercalation. Owing to not only the performance, but also the high price of LiCoO$_2$, lithium nickel oxide (LiNiO$_2$) thus becomes a new role. It has a large capacity with a high working voltage (15% higher by volume, 20% higher by weight) and is far cheaper. But it is not effective due to the electrolyte decomposition problems *(Thomas et al., 1984 and Linden (Ed.) et al., 1995)* and also less ordering *(Rougier et al., 1996)*, as compared to LiCoO$_2$. The addition of cobalt to LiNiO$_2$ increases the degree of ordering, leading to occupied sites by nickel ions in the nickel/cobalt plane rather than in the lithium plane *(Whittingham et al., 2004)*. Therefore, LiNi$_{1-x}$Co$_x$O$_2$, typically containing mostly nickel (x~0.8), has been used to take advantages of lower cost and higher capacity of nickel relative to cobalt *(Shi X. et al., 2009, Lee D.G. et al., 2009 and Baskaran et al., 2009)*. With LiNi$_{1-x}$Co$_x$O$_2$, cobalt helps reduce the amount of nickel in the lithium layer and small amounts of cobalt (up to 0.20–0.25) have been shown to improve capacity *(Li D. et al., 2008, Kosova et al., 2008 and Li J. et al., 2009)*. Although nickel in the lithium layer can be detrimental to lithium transport, it has been shown to stabilize the structure during delithiation and thus to improve cycling performance *(Rosciano et al., 2009)*. Another promising positive material is LiMn$_2$O$_4$ which forms a spinel structure (Fd3m), in which manganese occupies the octahedral sites and lithium predominantly occupies the tetrahedral sites *(Thackaray et al., 1993)*. The spinel lithium manganese oxide (LiMn$_2$O$_4$) has a high working voltage, high stability of the electrolyte and a very low price, but the discharge capacity is still too low and phase change can occur during the cycling. Thus, the addition of iron results in an additional discharge plateau at high voltages, while cobalt improves the capacity retention during cycling by stabilizing the spinel crystal

structure. However, the most common addition to $LiMn_2O_4$ is nickel *(Ohzuku et al., 1999)*, which decreases the lattice parameter and the electrical conductivity of $LiMn_2O_4$ *(Fang T.-T. et al., 2008)*.

The addition of nickel to the surface of $LiMn_2O_4$ through coatings, rather than as a bulk dopant, can also be effective in improving capacity retention during cycling *(Yuan Y.F. et al., 2008 and Lee J.-W. et al., 2009)*. Orthorhombic V_2O_5 and monoclinic LiV_3O_8 have been used as cathode materials. These electrodes have high capacities, but relatively low voltages (typically 3V or less) *(Sahana et al., 2009 and Benedek et al., 1997)*.

Another promising class of cathode materials is phosphates ($LiMPO_4$) with the olivine structure (Pnma). The most commonly used cathode is $LiFePO_4$, which delithiates to $FePO_4$ as the Fe^{2+} is oxidized to Fe^{3+} *(Padhi et al., 1997)*. The formation of a two-phase mixture establishes a fixed activity, resulting in a relatively flat discharge profile (i.e. the voltage remains relatively constant during discharge) *(Stewart S.G. et al., 2008)*. Conductivity can be improved by heat treatment to increase the conductivity *(Amin et al., 2008)*. Other phosphates used for cathodes in lithium ion batteries include $LiMnPO_4$ and $LiCoPO_4$. $LiMnPO_4$ and $LiCoPO_4$ have higher open circuit voltages (4.1 and 4.8 V, respectively) than $LiFePO_4$ (3.5 V) *(Whittingham et al., 2004)*, but have lower capacities.

For the anode materials of Li-ion battery, the most widely used electrode material is graphite although the theoretical capacity is limited to 372 mAh/g due to its highly negative working potential close to that of Li/Li^+, flat discharge performance, high-power availability, low initial charging capacity loss, and safety. There are still many materials that have high capacity, such as polyacenes, hard carbons, low-temperature mesophase carbons, silicon-containing carbons, metallic silicon, metal nitrides, etc., but all of them have some serious issues hindering actual use. Another interesting material is tin-based anode materials which was first initiated by Fuji Film Company in the mid-1990s, and later extended from oxides to alloys. Their advantages are ease of preparation (heat-treatment below 1500 °C or simple mechanical milling) and high volumetric capacity, which can be twice the volumetric capacity of carbonaceous anode materials *(Idota Y et al., 1997)*. Lithium transition metal nitrides were first proposed in the 1990s as alternative materials for

negative electrodes in lithium-ion batteries. $Li_{2.6}Co_{0.4}N$ has received much attention as a result of the very high specific capacity values that can be achieved (typically 700–800 mA· h/g) *(Shodai T. et al., 1997)* at somewhat higher voltages than those used for carbonaceous electrodes. LiNiN is coupled with metallic conductivity as Li is completely substituted by Ni between Li-N layers. These factors, showing the properties of LiNiN as electrode material in lithium-ion batteries, could be interesting. LiNiN were synthesized by heat treatment of Li_3N and nickel foil at 730–750 °C for 7 days, following a method described previously *(Stoeva Z. et al., 2007)*. The titanium oxide compounds are also applied for the negative electrode materials, for example, spinel $Li_{4/3}Ti_{5/3}O_4$. Spinel-type $Li_{4/3}Ti_{5/3}O_4$ or $Li_4Ti_5O_{12}$ (white crystal) can be used as anode material for lithium secondary batteries. Its structure is similar to that of spinel $LiMn_2O_4$. The compound is called zero-tension electrode material. The discharge process is very stable: the average voltage plateau is 1.56 V. Reversible capacity is about 150 mA h/g, only 10% less than the theoretical capacity of 168 mA h/g *(Peramunage D. et al., 1998)*.

2.3 Sol-gel Method for Electrode Materials Synthesis

Sol–gel method is the most promising technique since it provides many advantages over the conventional solid-state reaction, viz. homogeneous mixing at the atomic or molecular level, good stoichiometric control, low synthesis temperature, short-heating time, good crystallinity uniform particle size and small diameter, even down to nanometer level *(Klein L. et al., 1988 and Brinker CJ. et al., 1990)*. The principle of the sol-gel method is used to fabricate the materials as metal oxides. It starts from chemical solution to an integrated network (*gel*) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal chlorides, which undergo various forms of hydrolysis and polycondensation reactions. The formation of a metal oxide involves in connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges.

The positive materials, typically lithium cobalt oxide ($LiCoO_2$), lithium nickel oxide ($LiNiO_2$), lithium manganese oxide ($LiMn_2O_4$) and vanadium oxide (V_2O_5), can be prepared by the sol-gel method to improve the Li-ion battery

performance. Lithium cobalt oxide (LiCoO$_2$) can be prepared by the solid-state reaction, using a long heating time and high temperature to obtain uniform and good products since the diffusion coefficient of Li+ ions is not high, thus, the sol-gel method is preferable. A cobalt salt is dissolved in water and pH is adjusted with LiOH and aqueous ammonium solution to form a gel. During this process, control of the pH is very important. If it is not well controlled, precipitation will happen *(Wu YP et al., 2002)*. In order to control the particle size and uniformity of the products, an organic acid is added as a carrier. The carrier should have hydrophilic functional groups, such as hydroxides or carboxylates. Most common ones are small molecules like succinic acid, oxalic acid, malic acid, tartaric acid, acrylic acid, citric acid, humic acid, and polymers like poly(acrylic acid) (PAA) and poly(vinylpyrrolidone) (PVP) *(Yoshio M et al., 1992 and Kanga SG et al., 1999)*. The ratio of PAA to metal ions can be changed, but it should be enough to suppress cation mobility during the heat treatment. As the result, not only the size of the particles can be controlled at the nanometer level (in the range of 30–50 nm) and the specific BET surface area in the range of 2.3–17 m^2/g, but also the mixing can be completely uniform at an atomic level. The reversible capacity and cycling behavior of the obtained LiCoO$_2$ are superior to those from the solid-state reaction. The reversible capacity can be above 150 mAh/g, as compared to 120 mAh/g obtained from the solid-state reaction product, and 97% of the initial discharge capacity after 350 cycles is still retained *(Sun YK et al., 1999)*. However, LiCoO$_2$ synthesized at low temperature has an intermediate structure between layered and spinel structures, whose reversible capacity is low, about 80 mAh/g. This result shows that heat treatment at a high temperature is still necessary to obtain a good and stable layered structure *(Yoon WS et al., 1999)*.

Lithium nickel oxide (LiNiO$_2$) has a layered structure similar to LiCoO$_2$. It is cheaper than LiCoO$_2$ and its reversible capacity is higher than that of LiCoO$_2$, it is difficult to prepare on a large scale with an ideal layered structure. However, sol-gel method can be used to overcome this drawback. The general process of the sol-gel method is similar to that for the preparation of LiCoO$_2$. At first, lithium hydroxide and ammonium hydroxide are added to a nickel salt solution of, for example, nickel nitrate. After obtaining a gelatinous precipitate, the solvents are removed by

evaporation at temperatures below 100 °C. Then, the unreacted lithium compounds are removed by washing with water. The resulting dried powder is heat treated at a temperature above 400 °C to obtain crystalline $LiNiO_2$ *(Choi YM et al., 1998)*. The results shown the crystalline $LiNiO_2$ prepared by the above sol-gel methods displays good capacity retention. For example, after 350 cycles more than 90% of the initial capacity is retained.

Lithium manganese oxide ($LiMn_2O_4$), different from the previous positive materials, $LiCoO_2$ and $LiNiO_2$, has a spinel structure (AB_2X_4). Thin film $LiMn_2O_4$ electrodes can be prepared by the sol-gel method using anhydrous $Mn(CH_3COCHCOCH_3)_3$ (manganese acetylacetonate) and $Li(CH_3COCHCOCH_3)$ (lithium acetylacetonate) as precursors via spin coating and annealing processes *(Park YJ et al., 2000)*, or using the condensation polymer of citric acid and ethylene glycol as a carrier *(Wu YP et al., 2000)*. The structure of the obtained gel is changed with the ratio of the carriers to the Li+ and Mn3+ ions *(Sun YK et al., 1997)*, and it can be either crosslinked or non-crosslinked. As the results, the reversible capacity is up to 135 mAh/g (91% of theoretical capacity) and the capacity fading is very slow. With lithium metal as a reference electrode, after 168 cycles the capacity is faded only 9.5%, comparing with solid-state method. The optimum pH and molar ratio of the carrier to total metal ion content are 6.0 and 1.0, respectively *(Hwang BJ et al., 2001)*. $LiMn_2O_4$ can also be prepared directly from heating a gelatinous $LiMn_2O_4$ powder obtained by drying a sol from lithium acetate dihydrate, manganese acetate tetrahydrate and tartaric acid at 50 °C *(Pyun SI et al., 2003)*.

Another positive electrode material is vanadium oxide (V_2O_5). It can be prepared by the aqueous route via hydrolysis of vanadium oxide from vanadic acid, usually leading to ordered gels with a layered structure, but the hydrolysis of alkoxide precursor results in an amorphous structure *(Coustier F et al., 1997)*. αV_2O_5 has a layered structure with a distorted close-packed oxygen array. Three lithium ions can be inserted, finally arriving at the composition $Li_3V_2O_5$. Crystalline αV_2O_5 thin films can be prepared by the sol-gel route using vanadium oxo-isopropoxide as a precursor, followed by annealing at a low temperature (400 °C) *(Meulenkamp EA et al., 1999)*.

For the negative electrode materials, typically tin oxides, titanium oxides and their materials, they can also be synthesized by sol-gel method. Tin oxide and its materials can be prepared by directly slow hydrolysis of tin chloride by controlling the pH *(Wu YP et al., 1998)*, the non-hydrolytic sol–gel method *(Harreld JH et al., 2003)*, and the sol–gel method, using organic carriers *(Zhang R et al., 2002)*. The reversible capacities obtained are 500 mAh/g, 390 mAh/g, and 600 mAh/g, respectively, comparing to the commercial one which is 420 mAh/g. Tin oxide can be prepared by using tin-isopropoxide (10%, w/v) as precursor in *iso*-propanol (72 vol.%) and toluene (18 vol.%), giving nanocrystalline semiconductor SnO_x thin film having the thickness and the nanocrystallite size within the range of 100–150 nm and 6–8 nm, respectively *(Shukla S. et al., 2003)*.

Negative materials of titanium oxides include $Li_{4/3}Ti_{5/3}O_4$ spinel and TiO_2 anatase. $Li_{4/3}Ti_{5/3}O_4$ Spinel is similar to $LiMn_2O_4$ spinel and can be written as $Li[Li_{i1/3}T_{i5/3}]O_4$ with the space group Fd3m and a crystal parameter a = 83.6 pm. When using the sol-gel method, poly(ethylene glycol) or poly(vinylpyrrolidone) *(Kavan L et al., 2002 and Rho YH et al., 2004)* as a carrier is employed to hydrolyze titanium (IV) alkoxides with lithium salt, followed by an annealing to obtain nano-crystalline spinel-type $Li_{4/3}Ti_{5/3}O_4$. It exhibits excellent activity during lithium insertion even at a high charge rate of 250 °C. Nano-crystalline $Li_{4/3}Ti_{5/3}O_4$ prepared without carriers surprisingly presents an initial capacity of 272 mA h/g, greatly larger than its theoretic capacity *(Shen CM et al., 2002)*. TiO_2 anatase films can be prepared by a sol–gel technique with a subsequent hydrothermal growth of crystals in basic solutions. Hydrothermal treatment at 190–230 °C leads to the formation of compact films with a narrow pore size distribution *(Krtil P et al., 2000)*.

Other kinds of negative materials that can be prepared by the sol-gel method include WO_3, MoO_x, CrO_x, $LiFeO_2$, and graphite composite. There are also some interesting materials that can be used for electrode materials of Li-ion battery.

Transition metal-oxide spinels are important in many application fields because of their high thermal resistance, catalytic, electronic, and optical properties. They are commonly used in semiconductor and sensor technologies, as well as in heterogeneous catalysis *(Schmidt W et al., 2001 and Salavati-Niasari M et al., 2008)*;

and compounds with spinel-related structure also provide suitable host materials for insertion of lithium ions for electrode material of Li-ion battery application *(Eisenberg, M, J. 1980)*. The general formula of spinel compounds can be represented as AB_2X_4 with space group of *Fd3m*. The unit cell contains 32 X anions on the 32e sites (cubic close-packing arrangement), 8 A cations on 8a sites (tetrahedrally coordinated by anions), and 16 B cations on 16d sites (octahedrally coordinated). Nevertheless, A cations can also occupy 16d sites and some B cations 8a sites, to give an inverse spinel. It is also possible to find cation-deficient spinels, thus increasing the number of available sites for intercalation, for example, $CuInSnS_4$ by the solid-state method *(Dedryve're et al., 1999)* and $CuAl_2O_4$ by the sol-gel method *(Salavati-Niasari M. et al., 2009)*. $CuAl_2O_4$ by the sol-gel method using the Pechini method involves in combining a metal precursor with water, citric acid, and a polyhydroxyalcohol, such as ethylene glycol *(Pechini MP, 1967)*. The lowest temperature for preparation of the pure $CuAl_2O_4$ nanocrystals is about 800 °C. The morphology of as-prepared $CuAl_2O_4$ was quasi-spherical and the dimension was measured to be 17–26 nm. The band gap, Eg, was calculated at 2.10 eV by using the stimulated wavelength limit of $CuAl_2O_4$.

2.4 Electrospinning Technique for Metal Oxide Fiber

Electrospinning is a simple and versatile method for generating ultrathin fibers from a rich variety of materials, including polymers, composites and ceramics. This nonmechanical, electrostatic technique involves in the use of a high voltage electrostatic field to charge the surface of a polymer solution droplet, and thus to induce the ejection of a liquid jet through a spinneret. By combining the electrospinning with the sol–gel methods, design vesicles and nanofibers can be made, using inorganic oxides and hybrid (organic/inorganic) materials with diameters in the micrometer and submicrometer range *(Larsen G. et al., 2003)*. It was generally observed that the calcination temperature has a great influence on both the crystalline phase and the surface morphology of the fibers.

Typically, ceramic electrospinning involves in the following steps:

- Preparation of electrospinning solution.
- Electrospinning of the prepared solution into the polymer/inorganic composite fibers.
- Calcination of the composite fibers to remove unwanted constituents (polymer, solvent) and to obtain the oxide fibers.

Lanthanum nitrate/copper nitrate/polyacrylamide composite fibers were prepared by combining a sol-gel process and electrospinning. It use 5 -25 kV to generate the nanofiber and calcined at 600 °C *(Hyun P. 2005)*. Zirconium oxide/PVAc composite nanofibers were found to have smooth, uniform surfaces with various diameters in the 400–500 nm range. The fiber was calcined at 500–1000 °C *(Dharmaraj N. et al., 2006)*. $Fe(NO_3)_3$/PVA, $Co(NO_3)_2$/PVA, and $Ni(NO_3)_2$/PVA composite fibers have a uniform and smooth surface, with diameters of about 210, 180, and 220 nm, respectively. The precursor fibers heated to 500 °C under a heating rate of 10 °C/min for 4 h in an air atmosphere gave diameters of 40, 54, and 50 nm, respectively. The calcined nanofibers obtained were polycrystalline Fe_2O_3, CoO, and NiO, respectively *(Hui Wu et al., 2007)*.