学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　韓 成功

学 位 論 文 題 名

Development of High Performance Manganese-based Cathode Materials for Li-ion Batteries
(Li イオン電池のための高性能 Mn 系カソード用材料の開発)

Rechargeable *Li*-ion batteries are considered as one of the most effective devices for storing the renewable energies without air pollution. The urgent demands from the application markets, e.g. smart phones, laptops, electric vehicles, hybrid electric vehicles, require the development of high power/energy rechargeable *Li*-ion batteries, which are mainly determined by the relatively low capacity of cathode materials. *Mn*-based oxide cathode material, spinel $LiMn_2O_4$, is paid more attentions due to its low cost, no toxicity, environmental friendliness, relatively high energy density compared with the commercialized $LiCoO_2$. However, its further application is restricted by the serious capacity fading in cycling process, arising from the dissolution of manganese, Jahn-Teller distortion, and structural instability. In this work, three technologies, synthetic technology, doping technology, and surface modification technology, are proposed to overcome and alleviate the above problems. Solution combustion synthesis is employed as synthetic technology; *Bi* and *La* co-doping is chosen as doping technology; modifying a Mn^{4+}-rich phase, and a Li_2CuO_2-Li_2NiO_2 solid solution on the surface of $LiMn_2O_4$ particles is served as surface modification technology. In addition, another *Mn*-based oxide cathode material, *Li*-rich layered xLi_2MnO_3-(1-x) $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is also introduced and prepared due to its high capacity with the possible application in the future. This thesis includes 6 chapters, in which the first and last chapters are general introduction and general conclusion, respectively.

Chapter 2 shows the solution combustion synthesis of $LiMn_2O_4$ powders. Mixed fuels of glycine and sucrose with different molar ratios were used to produce the $LiMn_2O_4$ powders with sizes of 100 － 200 nm. The effects of different molar ratios of glycine to fuel on the phase structure, morphologies, yields, and electrochemical performance of final $LiMn_2O_4$ were investigated in detail. The presence of sucrose in the fuels was in favor of producing nanosized $LiMn_2O_4$ particles, improving yields, alleviating the explosive combustion reaction, and resulting in the nondecreasing electrochemical performance.

Chapter 3 presents doping technology for obtaining the high electrochemical performance of spinel $LiMn_2O_4$. *Bi* and *La* as doping elements were employed to prepare $LiBi_xLa_xMn_{2-2x}O_4$ materials. A substitution of *Mn* by *Bi* and *La* resulted in the enlarged lattice parameters, and more stable structure, which facilitated the fast diffusion of *Li*-ions, and cycling stability, respectively. A remarkably improved electrochemical performance of $LiMn_2O_4$ was observed due to the synergistic effect of *Bi* and *La* in spinel structure.

Chapter 4 displays surface modification technology for improving the electrochemical performance of spinel $LiMn_2O_4$. Two kinds of materials, a Mn^{4+}-rich phase, and a Li_2CuO_2-Li_2NiO_2 solid solution, were chosen as the surface modified materials. In this chapter, the modified amounts played a critical role on the phase structure, morphologies and electrochemical performance. The presence of a Mn^{4+}-rich phase alleviated the dissolution of manganese in the electrolyte, thus improving the cycling performance and rate capability relative to the bare $LiMn_2O_4$. In addition, when using a Li_2CuO_2-Li_2NiO_2 solid solution, the modified layer on the surface of $LiMn_2O_4$ particles, featuring a $LiNi_zMn_{2-z}O_4$-like phase as well as a Li_2CuO_2-Li_2NiO_2 solid solution, played a key role in alleviating the dissolution of manganese, thus enhancing the cycling performance and rate capability.

In Chapter 5, *Li*-rich layered xLi_2MnO_3-(1-*x*) $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ oxides were prepared by solution combustion synthesis using the mixed fuels of glycine and sucrose. Phase structure, morphologies, electrochemical performance were determined by *x* values. Different *x* led to the different electrochemical performances. For comparison, 0.4Li_2MnO_3-0.6 $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ oxide was also prepared by using glycine as the only fuel. Using different fuels led to the different phase structure, morphologies, and electrochemical performance.

The final goals for obtaining high electrochemical performance of *Mn*-based cathode oxides were reached.