

Combustion synthesis of Li–Mn spinel nanostructures as cathode materials for lithium–ion batteries

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In recent years, lithium–ion batteries have been considered as the most promising power sources of consumer’s electronic devices such as mobile phones and laptop computers. Common commercial cathode materials used in lithium–batteries are the compounds of transition metal oxides: LiCoO_2 (layered), LiMn_2O_4 (spinel), LiNiO_2 (layered) and LiFePO_4 (olivine). LiMn_2O_4 spinel nanostructure is of great interest as positive electrode, due to its low cost, simple preparation, environmental friendliness and good safety. However, this cathode material suffers from some limitations such as capacity fading during charge/discharge cycling. To overcome this problem, many researchers have tried to modify the material structure either by tuning the synthesis parameters or/and substituting a small amount of Mn ions by various ions of Co, Ni, Al, Mo, Cr etc. Recently, Kebede *et. al.* [1] synthesized pristine LiMn_2O_4 and Al-doped LiMn_2O_4 ($\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$) spinel cathode materials using a solution combustion method. The samples $\text{LiAl}_{0.05}\text{Mn}_{1.95}\text{O}_4$ and $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ exhibited higher discharge capacity for the first two cycles compared to the first cycle discharge capacity of pristine LiMn_2O_4 .

The combustion method involves the autoignition of an aqueous solution containing an oxidizer (the corresponding metal nitrates) and an organic fuel, such as urea. The resulting material characteristics, such as surface area and crystallite size, are strongly dependent on the fuel/oxidant ratio [2]. The combustion reaction is most vigorous and reaches high temperatures, when the fuel/nitrate molar ratio is close to its stoichiometric value, leading to large particles or agglomerates. Rapid evolution of a large volume of gases during the process cools immediately the product, limits the occurrence of agglomeration, thus leading to nanocrystalline powders.

In this work, we report on the physicochemical and electrochemical properties of LiMn_2O_4 spinel nanostructures prepared via the combustion method. Parameter of this study was the urea/nitrate ratio. $\text{Li}(\text{NO}_3)$ and $\text{Mn}(\text{NO}_3)_2$ were used as starting materials (oxidizing agents) and urea [$\text{CO}(\text{NH}_2)_2$] as fuel (reducing agent). $\text{Cu}(\text{NO}_3)_3$ was also employed as a precursor in the case of doped nanostructure. The materials were characterized by N_2 adsorption, X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), while electrochemical measurements (charge–discharge, cyclic voltammetry) were performed at ambient temperature by two–electrode cells including a positive electrode (LiMn_2O_4) as the working electrode and a Li foil as reference electrode and counter electrode (electrolyte: 1M LiPF_6 in EC/DMC). For comparison reasons, a commercial LiMn_2O_4 positive electrode was also employed.

References

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