Abstract

With the increasing demand and uninterrupted supply of energy to each sector with continual population and industrial growth, it has been necessary to search alternative new energy sources to fulfill the demand based energy supply. The rapid rate of depleting fossil fuel has opened a new era of intense research for alternative new energy sources. The research is focusing on the use of renewable energy sources. The use of these sources depends on the reliability and capacity of the energy storage system. There are various energy storage systems namely: electrochemical, biological, chemical, thermal, electrical, mechanical, etc. The electrochemical energy storage systems, e.g. batteries and supercapacitors, provide an alternate with the safe and easy operation. Lithium ion based batteries have high volumetric and gravimetric energy density, higher cell voltage, good cyclability, and longer self-life compared to lead acid battery.

The Li-ion battery is one of the potential energy storage systems for smart electronics gadgets and electric vehicle (EV), and it has been directed towards long lifetime and high safety. In particular, Li-ion battery performance for EV application declines steeply as the cycle life. Considerable research has been done in the last decade to identify novel cathode materials for high energy density Li-ion rechargeable batteries. Lithium ion battery is made of three parts: cathode, anode, and electrolyte. There are three types of lithiated oxides, found suitable for Li-ion rechargeable batteries namely (i) layered oxide materials (e.g $LiCoO_2$), (ii) spinel lithium manganese oxide (e.g. $LiMn_2O_4$), and (iii) open framework olivine compounds (e.g. $LiFePO_4$). Each of them has some drawbacks e.g. layered $LiCoO_2$ is toxic and expensive, spinel $LiMn_2O_4$ shows structural change upon cycling and olivine $LiFePO_4$ has very low electronic conductivity. It has already been reported that the charge-discharge characteristics and cyclability of $LiMn_2O_4$ can be improved by substituting the Mn^{3+} ion with transition metals e.g. Cr, Co, Fe, Ni, Cu, etc.

Most of the reported spinal cathode materials work in 4 V - 5 V range. These cathode materials are still facing capacity fading and cyclability issues which are becoming an obstacle for its commercial availability. The current research interest needs attention towards the development of new cathode, anode and electrolyte materials to make Li-ion battery technology commercially viable option. The rare earth doping could be one of the viable solutions for capacity fading and cyclability because it can keep the spinal structure in order by overcoming John Teller distortion and improving electronic conductivity. However, little attention was paid towards the rare-earth elemental doping and its effect on capacity and cyclability.

The different rare-earth metal doping showed the improved electrochemical behavior of lithium manganese oxide cathode materials. But, the field is not completely explored yet. In the present work, we decided to explore the effects of various rare-earth elements doping on electrochemical performances of $LiMn_2O_4$ cathode materials in an organized way. The work emphasizes on the synthesis of rare-earth elemental, Gd, Dy, Yb, Tb, Yb and Nd, doped cathode material via an organic-sol-gel method. Significantly, the initial discharge capacities for LMO-Gd04are 115.9, 93.9, 75.8, 47.3 mAh^{-1} at C/10, C/5, C/2, 1C respectively, superior to pristine LMO and Gd doped cathode materials. The capacity retention after 40 cycles is observed as 70.64% and 84.63% for LMO andLMO-Gd04,respectively. The initial charge-discharge capacities for the LMO-Dy02cathode are 154.0, 77.2, 74.4 and 124.7, 72.8, 77.8 $mAhg^{-1}$ at C/10, C/5 and C10 (recv.) rates. Similarly,the rare earth doping with Gd and Dy exhibit better cycling performance compare to pristine $LiMn_{1.5}Ni_{0.5}O_4$. After 55 cycles at C, the discharge capacity values are recorded as 104 $mAhg^{-1}$, 84.7 $mAhg^{-1}$ and 74.1 $mAhg^{-1}$ for $LiMn_{1.48}Ni_{0.5}Gd_{0.02}O_4$, $LiMn_{1.46}Ni_{0.5}Dy_{0.04}O_4$, and $LiMn_{1.5}Ni_{0.5}O_4$ respectively.

In brief, the work emphasizes on the synthesis of rare-earth elemental, (Gd, Dy, Yb, Tb, Yb and Nd) doped cathode material via an organic sol-gel method. The synthesized materials were found to work in 4 V - 5 V potential ranges.

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