UDC 544.6.076.324.4 + 544.016

ELECTROCHEMICAL PROPERTIES OF $LiMn_2O_4$ SURFACE-MODIFIED WITH $LiNi_{0.5}Mn_{1.5}O_4$

POTAPENKO A.V
Joint Department of Electrochemical Energy Systems,
38a Vernadsky Blvd., Kiev 03680, Ukraine
avoloshka@ukr.net

Surface modified samples of $LiMn_2O_4$ coated with $LiNi_{0.5}Mn_{1.5}O_4$ have been synthesized by a citric acid aided method and tested as a cathode material in sample lithium ion batteries. It has been been found that the surface layer of $LiNi_{0.5}Mn_{1.5}O_4$ is easily permeable for Li^+ ions. The surface modified samples are able to endure current loads of 20C (2940 mAh/g) without degradation and after heavy-duty tests deliver the same specific capacity as before current loading.

The growing need in renewable energy storage is enhancing the research on new materials and the ways of their improvement. Nowadays, substituted lithium manganese spinels are used as cathode materials for rechargeable lithium ion batteries due to their low cost and high potential vs. Li/Li^+. These are promising for numerous applications, in spite of capacity fading upon cycling, which hinders their commercialization. In view of this fact, numerous methods of enhancing their properties have been suggested. One of them is based on the surface modification of the electrode material [1]. In this case, the composition of a solid layer formed on the surface of the mother material is changing, and less degradation of the electrode and electrolyte solution occurs.

In our recent papers, two types of lithium manganese spinels, $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$, have been studied in one and the same electrolyte, viz. a 1 mol/L solution of $LiPF_6$ in a mixture of ethylene carbonate/dimethyl carbonate with a mass ratio of 1:1 [2-4]. It has been found that in spite of a considerably higher working potential range of the latter material, it is extremely stable on cycling even at high current loads.

Therefore, the aim of this work was to obtain the lithium manganese spinel coated with $LiNi_{0.5}Mn_{1.5}O_4$. It might be helpful in achieving more efficient cycling of the electrode material due to the presence of a protective “shell” on the surface of the stoichiometric lithium manganese spinel.

Research Methodology

Materials under investigation were synthesized by the citric acid aided procedure described in Refs. [5,6] using solutions of lithium nitrate, nickel (II) nitrate, manganese (II) nitrate, and citric acid (all of analytical grade) mixed in proper molar ratios. In order to modify their surfaces, a pyrolysed precursor of $LiMn_2O_4$ was soaked with the solution containing lithium, nickel, manganese nitrate, and citric acid, so as to obtain a layer of $LiNi_{0.5}Mn_{1.5}O_4$ on its surface after pyrolysis. The mass ratio of $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ was adjusted to 1:0.1. The temperatures of pyrolysis and further annealing of pyrolysed samples were 400 °C and 700 °C, respectively. For more details of the procedure see our Refs. [2-4].

Electrochemical measurements were performed in model CR2016 coin cells on a home-made automated electrochemical workstation using cyclic voltammetry (CV) and galvanostatic charge/discharge cycling methods. Cells with a lithium metal anode serving as a counter and reference electrode, a cathode made of the material in question, a Celgard 2500 separator membrane, and a 1 mol/L solution of $LiPF_6$ in a mixture of ethylene carbonate/dimethyl carbonate with the mass ratio of 1:1 were assembled in a dry glove box. The working electrodes were made of 82% of the material under consideration, 10% of a conducting additive and 8% of a poly(vinylidene difluoride) binder.

Results and Discussion

In Fig. 1, CV curves for neat $LiMn_2O_4$, $LiMn_2O_4$ modified with $LiNi_{0.5}Mn_{1.5}O_4$, and neat $LiNi_{0.5}Mn_{1.5}O_4$ are compared. The data for neat spinels well correspond to those published [2,3]. The surface modified material perfectly reproduces the features of the neat $LiMn_2O_4$. The presence of $LiNi_{0.5}Mn_{1.5}O_4$ on the surface of the lithium manganese spinel is recognizable as reversible waves at potentials around 4.4-4.9 V.

Galvanostatic charge/discharge cycling data within the 3.5-4.5 V voltage range reveal that the surface modified samples behave like the samples of the neat $LiMn_2O_4$. This means that the surface layer of $LiNi_{0.5}Mn_{1.5}O_4$ is easily permeable for Li^+ ions. Clearly, much work should be done in order to determine the role of the modifier and changes in the resistance of $LiMn_2O_4$ after covering with $LiNi_{0.5}Mn_{1.5}O_4$. However, the dependence of capacity retention on the current load presented in Fig. 2 reveals that the surface modified samples are able to endure the current loads of 20C (2940 mAh/g) without degradation and after heavy-duty tests deliver the same specific capacity as before current loading.

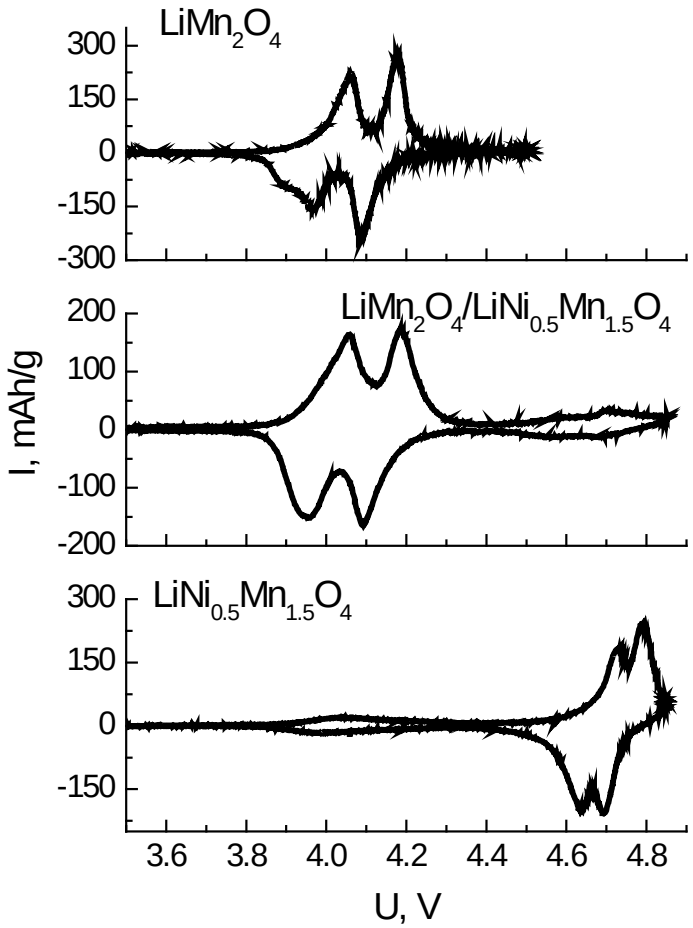

***Figure 1**. Cycling voltammograms for $LiMn_2O_4$, $LiNi_{0.5}Mn_{1.5}O_4$, and surface modified sample $LiMn_2O_4/LiNi_{0.5}Mn_{1.5}O_4$.*

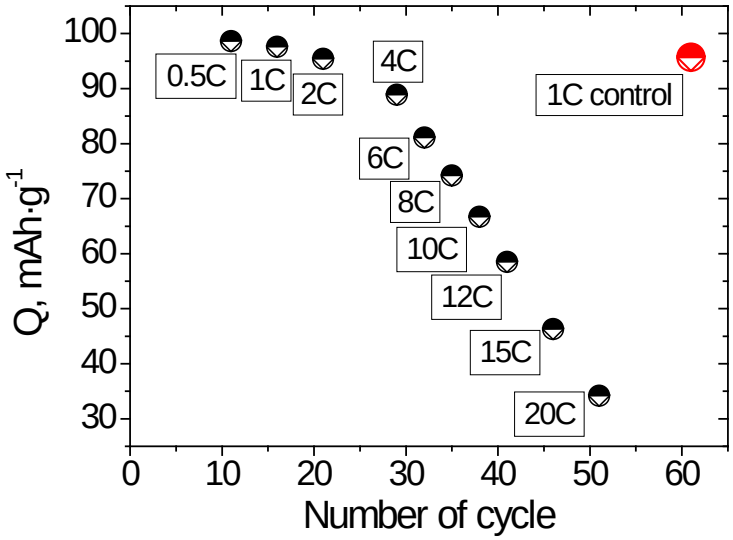

***Figure 2**. Dependence of discharge capacity on cycle number for the surface modified $LiMn_2O_4/LiNi_{0.5}Mn_{1.5}O_4$ sample. Numbers in the figure mean current loads in C units (1C=147 mAh/g)*

Conclusions

The surface modified samples of $LiMn_2O_4$ coated with $LiNi_{0.5}Mn_{1.5}O_4$ have been synthesized by a citric acid aided method. Electrochemical tests reveal that the surface layer of $LiNi_{0.5}Mn_{1.5}O_4$ is easily permeable for Li^+ ions. The surface modified samples are able to endure the current loads of 20C (2940 mAh/g) without degradation and after heavy-duty tests deliver the same specific capacity as before current loading.

Acknowledgments

The author is grateful to Dr. S.A. Kirillov for discussions, advice and comments.

References

[1] Z. Chen, Y. Qin, K. Amine, Y.-K. Sun, Role of surface coating on cathode materials for lithium-ion batteries, Journal of Materials Chemistry, 20, 7606–7612 (2010).

[2] A.V. Potapenko, S.I. Chernukhin, I.V. Romanova, K.Sh. Rabadanov, M.M. Gafurov, S.A. Kirillov, Citric acid aided synthesis, characterization, and high-rate electrochemical performance of $LiNi_{0.5}Mn_{1.5}O_4$, Electrochimica Acta, 134, 444-449 (2013).

[3] A.V. Potapenko, S.I. Chernukhin, S.A. Kirillov, A new method of pretreatment of lithium manganese spinels and high-rate electrochemical performance of $Li[Li_{0.033}Mn_{1.967}]O_4$. Materials for Renewable and Sustained Energy 3, 40-47 (2014).

[4] A.V. Potapenko, S.I. Chernukhin, I.V. Romanova, K.Sh. Rabadanov, M.M. Gafurov, S.A. Kirillov, High-rate Electrochemical Performance of Nanosized $LiNi_{0.5}Mn_{1.5}O_4$, International conference «Nanomaterials: Application and Properties (NAP-2013)», Sumi, Ukraine, 2, 04NEA06 (4 pp) (2013).

[5] I.A. Farbun, I.V. Romanova, T.E. Terikovskaya, D.I. Dzanashvili, S. A. Kirillov, Complex formation in the course of synthesis of zinc oxide from citrate solutions, Russian Journal of Applied Chemistry, 80, 1773-1778 (2007).

[6] I.A. Farbun, I.V. Romanova, S.A. Kirillov, Optimal design of powdered nanosized oxides of high surface area and porosity using a citric acid aided route, with special reference to ZnO, Journal of Sol-Gel Science and Technology, 68, 411-422 (2013).