

Response to Reviewer's comments

The manuscript 712458 entitled "Study on the synthesis of well-shaped Mn_3O_4 nanooctahedrons and their good performance for lithium ion batteries" had been submitted for publication in the journal Energies. It is devoted to the development of electrode material for Li-ion batteries having advanced characteristics. This class of materials is of great interest and importance nowadays. There are some comments related to the contents of the manuscript.

In the head of the paper the authors should point the type of their paper (Article, Review, Communication, etc)

Response: Thanks for reviewer's suggestion. The type of this paper is "Article", we have revised it in the revised manuscript. The revised contents have been marked with blue fonts.

The authors presented in the manuscript the CV data of the studied electrodes at a constant potential scan rate. It is reasonable to present series of CV curves measured at variation of potential scan rate in order to evaluate limiting stage of current determining process. Then it is advisable to analyze peak current values depending on potential scan rate, and try to use for this purpose Randles-Shevchik equation, as it is likely the mass-transport is the limiting stage of the electrochemical process. The authors should plot the dependencies of current density versus square root of potential scan rate of studied system. The linearity of such dependencies will prove the applicability of Randles-Shevchik equation in certain scan rates domain.

Response: Thanks for reviewer's suggestion. During the cyclic voltammetric measurements, Randles-Shevchik equation can be used to investigate the effect of potential scanning rate to the oxidation/ reduction peak current. We agree that series of CV curves measured at variation of potential scan rate can be used to evaluate limiting stage of current determining process. But for the performance evaluation of lithium-ion battery (LIBs), cyclic voltammetry is mainly used to study the redox mechanism that occurs during the charging and discharging process, which can provide the details of lithium insertion-extraction process. Normally the potential scan rate is set to 0.1 mV s^{-1} . We concede that the mass-transport is the limiting stage of the electrochemical process, but that is not the research focus of this work. The diffusion barrier of electrolyte ions can be studied by Nyquist plot of electrochemical impedance spectroscopy (EIS). In the revised manuscript, the EIS of two samples were supplied and analyzed. Even so, we are very grateful to the reviewer's suggestions.

Also it is reasonable to check the influence of activity coefficients of ions on the diffusion coefficient values. For this purpose, an approach can be applied developed for the solid state ionic transport in the intercalation materials described in the following papers: Russ. J. Electrochem. 55 (2019) 719-737; Ionics 22 (2016) 483-501; Electrochim. Acta 122 (2014) 187-196.

Response: Thanks for reviewer's suggestion. We have carefully read the above three papers, these paper provide comprehensive strategy to investigate and evaluate the Lithium diffusion and transport processes. The above papers have been cited in our revised manuscript, the

related electrochemical methods, calculation formula and evaluation systems will be adopted by us in the following research (Page 8, Line 286: Ref. 66-68.). These electrochemical methods and calculation equations are the most direct and clear quantitative analysis means. Thanks for reviewer's recommendation.

It is recommended to the authors to make additional EIS measurements. It is advisable to use for their analysis the equivalent circuit containing elements with clear physical meaning, which fit to this class of materials. The authors can find appropriate circuit in the following papers: J. Electroanal. Chem. 821 (2018) 140-151; Russ. J. Electrochem. 53 (2017) 706-712. This circuit is versatile enough to analyze impedance spectra of various electrochemical systems. It is obligatory to present calculated spectra at the same figure with experimental ones. All impedances should be presented as specific values /cm², calculated per total working surface of the electrode. For all fitted spectra calculated circuit parameters should be presented and discussed. It is strongly recommended to indicate frequencies of selected points at the figure with the spectra to make a notion regarding frequency domains of each spectra. It is also advisable to evaluate ionic diffusion coefficient in the material using modified Warburg formula, such an example the authors can find in the following papers: Ionics 22 (2016) 483-501; Electrochim. Acta 230 (2017) 479-491.

Response: Thanks for reviewer's suggestion. The papers "J. Electroanal. Chem. 821 (2018) 140-151; Russ. J. Electrochem. 53 (2017) 706-712." have been cited in the revised manuscript (Page 9, Line 328: Ref. 78-79). These papers will be helpful to enrich and improve the quantitative analysis and evaluation to the experimental data, and will be adopted by us in the following research.

In the revised manuscript, the electrochemical impedance spectroscopy (EIS) was supplied and used to investigate the Mn₃O₄ electrodes. It can supply related information to compare the electrochemical, electron and ion transport properties of different electrode materials. The Nyquist plots as well as the equivalent electrical circuit for the prepared two Mn₃O₄ electrodes were shown in Fig. 10a. The high frequency intercept on the real axis corresponds to the ohmic resistance (R_s), which originated from the electrolyte resistance, internal resistance of electrode, and contact resistance. The results indicated that the R_s values of the mixture of MnOOH/Mn₃O₄ and pure Mn₃O₄ electrodes are 2.1 and 2.5 Ω respectively. The semicircle in the high frequency region of Nyquist plot corresponds to charge-transfer resistance (R_{ct}). For the Mn₃O₄ nano-octahedrons electrode, the smaller diameter suggests that Mn₃O₄ nano-octahedrons possess a much lower charge transfer resistance (267.6 Ω) than that of the formed MnOOH/Mn₃O₄ (304.2 Ω). In addition, the slope of Nyquist plots in the low-frequency range of the EIS spectra correlates with the diffusion barrier of electrolyte ions. For Mn₃O₄ nano-octahedrons electrode, the much larger slope at low frequency intimated the faster electrolyte ion transfer than that in MnOOH/Mn₃O₄ electrodes (Fig. 10b). The supplied content has been marked with blue fonts in the revised manuscript (Page 9-10, Line 326-342.).

In the latter one the authors can find several approaches to study electrochemical kinetics of the materials able to maintain rapid charge and discharge processes. It is advisable also to compare results obtained using standard and modified Warburg formula. The high rate charge transport is key factor for modern electrode materials. The class of solid state compounds

which is called MAX-phases possess extremely high electroconductive properties. Also it improves cycling performance of Li-ion transport. It is reasonable to provide some short review in the Introduction section concerning examples of application of such compounds for enhancement of electroconductive properties of various electrode materials. The authors can find such an example in the following paper: Monatsh Chem 150 (2019) 489-498.

Response: Thanks for reviewer's suggestion. We have read the paper "paper: Monatsh Chem 150 (2019) 489-498.", it has been cited in the revised manuscript (Page 9, Line 328: Ref. 80). The electrochemical method and calculation equations will be helpful to our following working. Thanks for reviewer's recommendation.

After mentioned modifications the manuscript can be published in the journal Energies.

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