

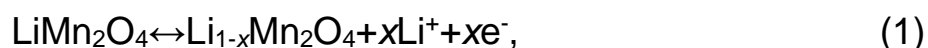
## COMPOSITION OF INTERMEDIATE PHASES SHOWING UP UPON DELITHIATION OF LITHIUM-MANGANESE SPINEL

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An analysis of voltammetric data for  $\text{LiMn}_2\text{O}_4$  has been performed, so as to recognize the possible presence of the intermediate phases. It has been found that in charge/discharge processes, in addition to the well-known  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$  phase,  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$  is easily identifiable, and its presence may be a key for understanding the properties of  $\text{LiMn}_2\text{O}_4$ .

Lithium manganese spinel,  $\text{LiMn}_2\text{O}_4$  is a cheap, environmentally benign alternative to currently employed  $\text{LiCoO}_2$  as a cathode in lithium ion batteries. Being able to operate at discharge currents of  $14800 \text{ A}\cdot\text{g}^{-1}$  [1,2], this material has good prospects for using in high-rate applications. Reversible electrochemical deinsertion of lithium ions from  $\text{LiMn}_2\text{O}_4$  takes place within the potential range of 3.0-4.5 V in accord with the following equation



with the theoretical capacity of  $148 \text{ mAh}\cdot\text{g}^{-1}$ , and leads to  $\text{MnO}_2$ . The structure of  $\text{LiMn}_2\text{O}_4$  is cubic ( $Fd\bar{3}m$ ,  $Z=8$ ) [3-4] with lithium ions occupying the tetrahedral (8a) positions, manganese ions ( $\text{Mn}^{3+}/\text{Mn}^{4+}$ ) in the octahedral positions (16d), and lithium ions inhabiting the tetrahedral (32e) positions and forming the cubic dense packing. Being separated from their neighbors by voids (16c), lithium ions have three-dimensional channels (8a–16c–8a–16c) for possible insertion, deinsertion and transport.

Structure transformations upon lithiation/delithiation are studied in great detail and may serve a key for better understanding the processes occurring in the spinel lattice. Both voltammetric and galvanostatic studies reveal a two-stage charge/discharge process enabling one to suggest the presence of an intermediate compound with  $x=0.5$ ,  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$  [5-8]. Significant efforts have been undertaken so as to describe the structure of the  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$  intermediate. As follows from Ref. [8], this phase belongs to the modulated  $R\bar{3}m$  space group,  $Z=6$ , with  $\text{O}^{2-}$  in the 6c and 18h positions,  $\text{Mn}^{3+}$  in the 3b positions,  $\text{Mn}^{4+}$  in the 9e positions, and  $\text{Li}^+$  partially filling 6c sites.

It has been found, however, that the aforementioned structures do not cover a wide variety of structural transformations occurring in  $\text{LiMn}_2\text{O}_4$  upon delithiation. Studying delithiated  $\text{LiMn}_2\text{O}_4$  single crystals by means of X-ray diffraction, Bjork et al. [7] have revealed that several superstructures may coexist in the samples. Continuing such investigations [8] they have concluded that among modulated phases belonging to these superstructures,  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$ ,  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$ , and  $\text{Li}_{0.25}\text{Mn}_2\text{O}_4$  can be present, and  $\text{Li}_{0.25}\text{Mn}_2\text{O}_4$  and  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$  structures can be derived as superlattices of the adjacent  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$  lattice. At that same time, in electrochemical studies of  $\text{Li}^+$  extraction from and insertion into  $\text{LiMn}_2\text{O}_4$  single crystal, Docco et al [9, 10] have observed a new peak at 3.86 V, which has not been reported previously for polycrystalline samples and possibly corresponds to a new intercalation phase.

In this work, an analysis of voltammetric data for the lithium manganese spinel has been performed, so as to recognize the presence of the intermediate phases described above. To do so, cyclic voltammetric curves have been treated as a set of closely overlap lines, and a method suggested in Ref. [11] for decomposing such lines has been employed. It appears that in charge/discharge processes,  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$  is easily identifiable, and its presence may be a key for understanding the properties of  $\text{LiMn}_2\text{O}_4$ .

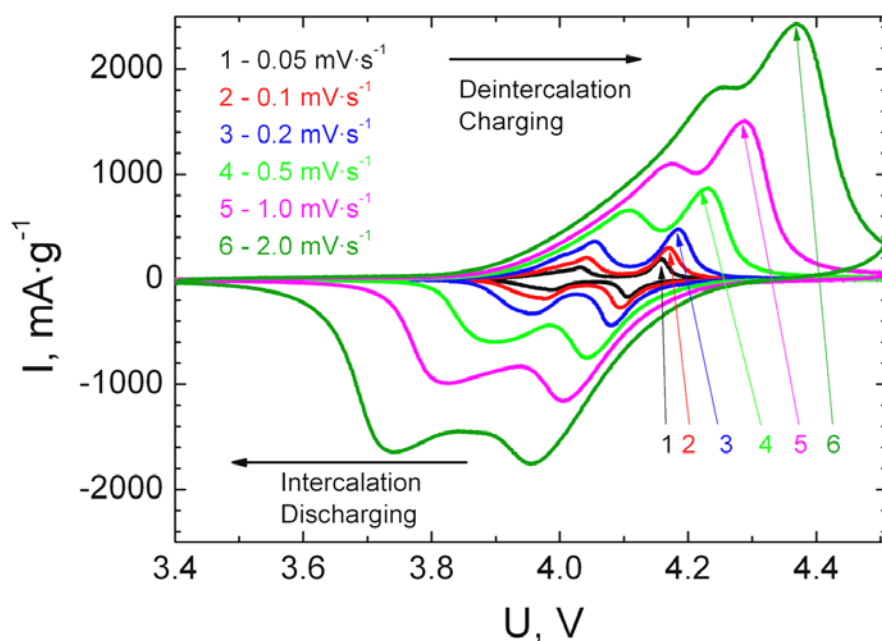
### **Research Methodology**

The stoichiometric lithium-manganese spinel  $\text{LiMn}_2\text{O}_4$  was synthesized by the citric acid route, which was described in previous papers. CR2016 coin cells were made to obtain electrochemical characteristics of the synthesized materials. Cyclic voltammetry (CV) was performed on a home-made automated electrochemical workstation. The “dry” component ratio of the analyzed material, the conductive additive, and the PVdF binder for the cathodes was 82:10:8. The cells were assembled in a dry glove box and consisted of a cathode made from the synthesized material, a lithium metal anode used as a counter and reference electrode, a Celgard 2500 separator membrane, and 1 mol/L solution of  $\text{LiPF}_6$  in the 1:1 mass ratio mixture of EC and DMC.

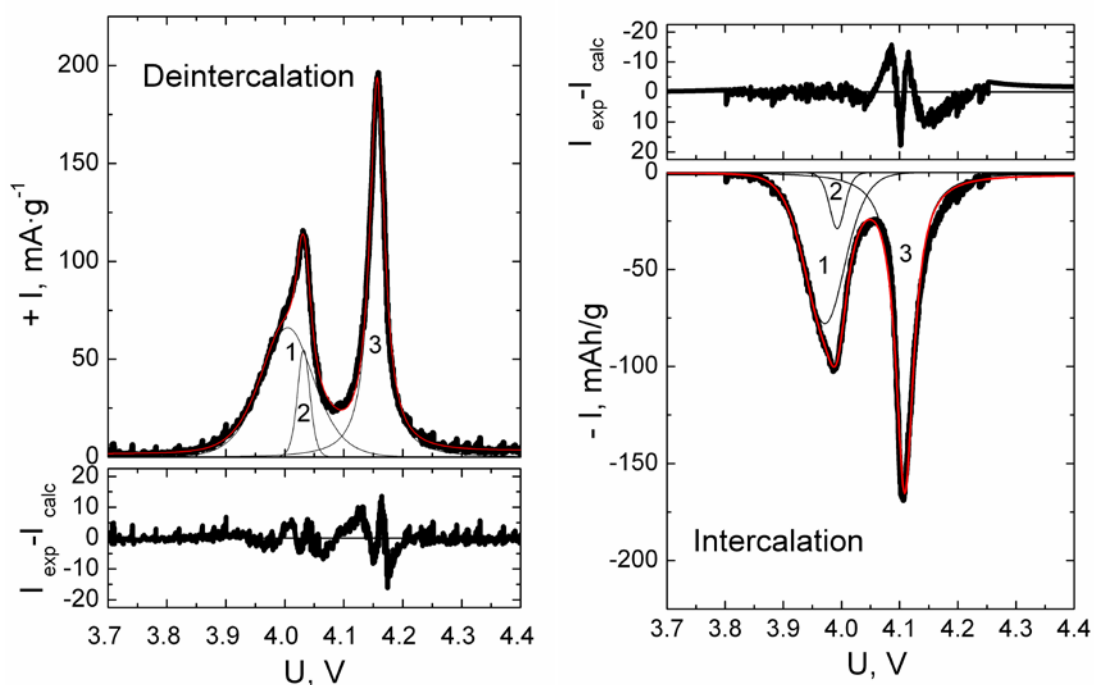
### **Results and Discussion**

Typical cyclic voltammetric curves for  $\text{LiMn}_2\text{O}_4$  obtained at various scanning rates are plotted in Fig. 1. A representative example of data fits is shown in Fig. 2. Cathodic and anodic curves have been treated separately. Composite voltammetric curves can be well represented by three severely overlap symmetric profiles, and a two-wave approximation undoubtedly fails. In what follows we enumerate the fitted waves from lower to higher potentials as 1, 2 and 3; in Fig. 2 these are situated at ca.

4.00, 4.03 and 4.16 V, respectively. Overlapping signifies that the previous processes still proceed when the next processes already run.



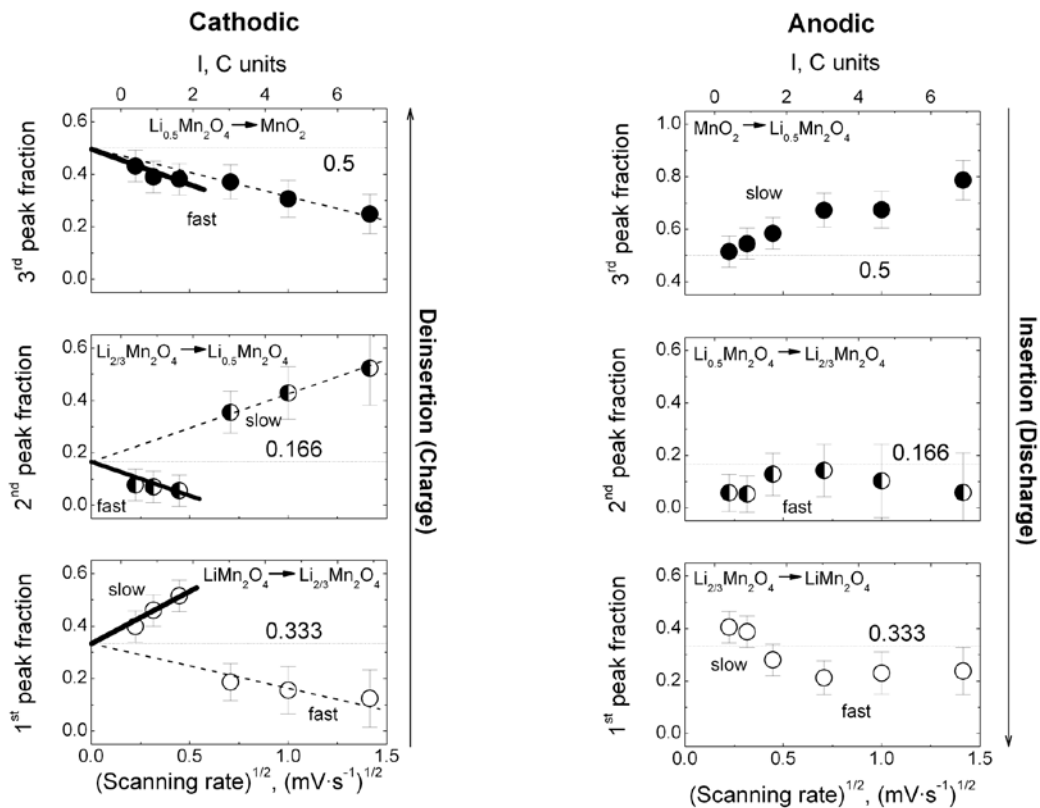
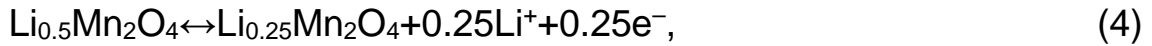
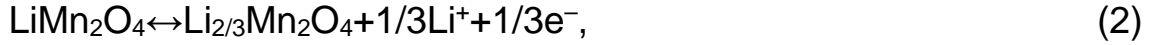
**Fig. 1.** Cyclic voltammetric curves for  $\text{LiMn}_2\text{O}_4$  registered at various scanning rates.



**Fig. 2.** Data fits for the cathodic and anodic waves of  $\text{LiMn}_2\text{O}_4$ .

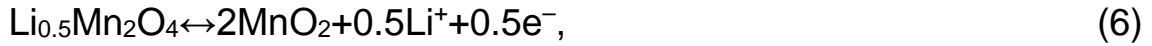
First of all, it is interesting to check if waves 1, 2 and 3 could correspond to the formation of intermediates predicted for  $\text{LiMn}_2\text{O}_4$  by

Björk et al. [7,8]. An analysis of capacities stored/delivered on charging/discharging processes shows that the transformation of  $\text{LiMn}_2\text{O}_4$  to  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$  and backwards requires  $0.366Q$ , Eq. (2) (we remind that  $Q$  is the theoretic capacity value), the conversion of  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$  to  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$  or the reverse reaction need  $0.134Q$ , Eq. (3), and further two-step delithiation of  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$  to  $\text{Li}_{0.25}\text{Mn}_2\text{O}_4$  and then to  $\text{MnO}_2$  or similar two-step lithiation of manganese dioxide necessitate  $2 \times 0.25Q$ , Eqs. (4), (5).



**Fig. 3.** Distribution of specific capacity between three cathodic peaks for  $\text{LiMn}_2\text{O}_4$  at various scanning rates.

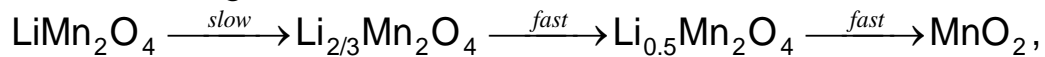
Respective dependences of capacity fractions (peak areas normalized to experimental specific capacities) on the scanning rate are plotted in Fig. 3. It is well seen that at the zero scanning rate, these dependences tend to the values predicted for  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$  and  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$ , whereas the presence of  $\text{Li}_{0.25}\text{Mn}_2\text{O}_4$  is indistinguishable suggesting that reactions (4) and (5) occur in one step,



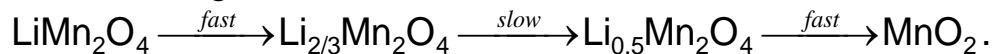
Of course, it is possible to perform calculations in terms of four composite waves, so as to reproduce a missing  $\text{Li}_{0.25}\text{Mn}_2\text{O}_4$  phase but we prefer to keep the parameterization of our calculations at the lowest possible level. On the other hand, one may safely state that the  $\text{Li}_{0.25}\text{Mn}_2\text{O}_4 \leftrightarrow \text{MnO}_2$  process, if exists, meets no kinetic limitations, and the  $\text{Li}_{0.25}\text{Mn}_2\text{O}_4$  phase is indiscernible in voltammetric experiments. Another point to stress is the greater the scanning rate, the greater the departure from Eqs. (2), (3), (6).

Analyzing the dependences of the peak fractions on the scanning rate enables one to draw qualitative conclusions regarding lithiation/delithiation kinetics. For all the three deinsertion waves, two different dependences on the scanning rate converging to a single point can be discerned, one for lower scanning rates and the other for higher ones, see the left hand side of Fig. 3 from bottom to top. It is a remarkable feature of these dependences for the deinsertion process that the first peak fraction reaches the theoretical value from above, while the second and the third ones from below. At lower scanning rates, the amounts of  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$  and  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$ , as follows from respective peak areas, are lower than expected, and an excess of  $\text{LiMn}_2\text{O}_4$  remains in the system. This may signify that  $\text{Li}^+$  extraction from  $\text{LiMn}_2\text{O}_4$  meets kinetic hindrances; the transformation of  $\text{LiMn}_2\text{O}_4$  to  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$  is slow and serves as a bottleneck for the  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4 \rightarrow \text{Li}_{0.5}\text{Mn}_2\text{O}_4$  and  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4 \rightarrow \text{MnO}_2$  processes, which are of commensurable rates. At higher scanning rates, the amounts of  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$  appear lower than expected, and an excess of  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$  accumulates in the system. One may guess that in this case, the transformation of  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$  to  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$  is the slowest. These relations may be described by the following schemes, which may signify that at different currents applied, ionic transport is carried out through different pathways:

slow scanning rates:



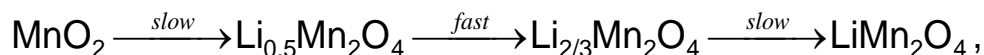
fast scanning rates:



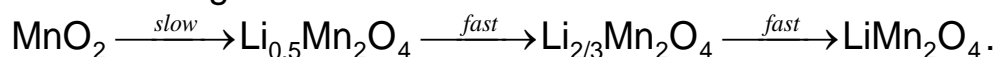
Unlike the deinsertion waves, the dependences of peak areas on scanning rate for the insertion waves demonstrate less distinct peculiarities. Examining the right hand side of Fig. 3 from top to bottom one may conclude that upon growing discharge rate, the 3<sup>rd</sup> peak fraction is greater than expected, and an excess of  $\text{MnO}_2$  remains in the system.

This may signify that the transformation of  $\text{MnO}_2$  to  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$  is kinetically restricted. The 2<sup>nd</sup> peak fraction is smaller than expected, and the transformation of  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$  to  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$  is fast. The 3<sup>rd</sup> peak fraction suggests that at slow scanning rates the transformation of  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$  to  $\text{LiMn}_2\text{O}_4$  is fast, and at fast scanning rates it is slow,

slow scanning rates:



fast scanning rates:



These findings are summarized in Table 1.

**Table 1.** Dependences of peak fractions on scanning rate for insertion/ deinsertion processes

	Delithiation		Lithiation	
	slow scan rate	fast scan rate	slow scan rate	fast scan rate
$\text{LiMn}_2\text{O}_4$	slow	fast	-	-
$\text{Li}_{2/3}\text{Mn}_2\text{O}_4$	fast	slow	slow	fast
$\text{Li}_{0.5}\text{Mn}_2\text{O}_4$	<b><u>fast</u></b>	<b><u>fast</u></b>	<b><u>fast</u></b>	<b><u>fast</u></b>
$\text{MnO}_2$	-	-	slow	slow

## Conclusions

In addition to the assumption regarding possibly different pathways accessible for ionic transport at different currents applied, one may infer that (i) forward and backward electrochemical reactions do not have the same rates and limiting stages, (ii) both lithiation and delithiation of  $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$  are fast and therefore (iii) lithiation and delithiation of  $\text{Li}_{2/3}\text{Mn}_2\text{O}_4$  are the rate-determining step of both charge and discharge processes.

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