Journal of Power Sources 276 (2015) 382–387

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

New high-voltage step at 4.8 V in cobalt free manganese based lithium phospho olivines for lithium-ion batteries

M. Memm*, M. Koentje, P. Axmann, M. Wohlfahrt-Mehrens

ZSW – Zentrum für Sonnenenergie- und Wasserstoff- Forschung Ulm, Baden-Württemberg, GB Helmholtzstraße 8, D-89081 Ulm, Germany

HIGHLIGHTS

- We synthesize Li metal phosphates with bivalent metals Fe, Mn, Ni, Mg.
- We find a new voltage step at 4.8 V for Mn–Mg and Mn–Ni containing samples.
- For Mg–Mn phosphates the discharge capacity clearly exceeds the $Mn^{2+/3+}$ step.

ARTICLE INFO

Article history:
Received 24 April 2014
Received in revised form
22 August 2014
Accepted 1 September 2014
Available online 6 October 2014

Keywords:
Materials science
Lithium ion batteries
Phospho olivine
$LiMnPO_4$

ABSTRACT

A new voltage step at 4.8 V can be activated in manganese based cobalt free phospho olivines by activating the utilisation of the $Mn^{3+/4+}$ redox pair applying Mg^{2+} as a Li^+-storage agent. CCCV cycling reveals a significant excess in discharge capacity of Mn–Mg co-containing samples related to the theoretical single electron step of $Mn^{2+/3+}$ and the occurrence of a new potential step at 4.8 V. These phenomena are not observed in Mg- or Mn-free samples even after charging them up to 5.3 V vs. Li/Li^+. Similar observations are made for Ni–Mn containing samples. Mg–Mn containing cathode materials can be a first step towards cobalt free high voltage phosphates for Lithium Ion batteries.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Energy storage is one of the main challenges of our time. Visions of future mobility and renewable energy all include new storage concepts. Among these Lithium Ion Batteries are one of the most promising candidates.

$LiMnPO_4$ is a highly attractive candidate for the use as active material in Lithium Ion cells. The material combines high safety in the charged state with an energy density comparable to the commercially used materials and low raw material costs.

$LiMnPO_4$ belongs to the class of the lithium transition metal phospho olivines $LiMPO_4$, firstly described by Padhi et al. [1]. The redox process for this class is expressed by the formula:

$$LiM^{2+}PO_4 \leftrightarrows Li^+ + e^- + M^{3+}PO_4$$

For $LiMnPO_4$ the electrochemical utilisation, the cycle stability and the rate capability are still poor. For pure materials only few publications report high capacity values of about 140–160 mAh g^{-1} [5,7,25,28,34]. Slow lithium diffusion kinetics, low electronic, and polaronic conductivity, a high structural strain at the phase boundary between charged and discharged phase and the structure destabilising effects of the Jahn Teller ion Mn^{3+} are discussed [1,3,6,7,9,10,16,18,21]. Furthermore a high energy barrier for the lithium transition through the crystal surface and instability of the delithiated state $Mn^{3+}PO_4$ are reported [22,27]. Nano sizing, partial substitution and application of conductive coatings have been proven to be effective techniques to improve the electrochemical behaviour [5,8,15,23,24,26,29,39,40]. Synthesis method and electrode preparation play an important role.

Partial substitution of manganese for divalent ions has also been described as a useful concept. Improved kinetics of $LiMnPO_4$ have been observed substituting small amounts of Mg^{2+} for Mn^{2+} [14]. Electrochemical active transition metals replacing manganese ions in $LiMnPO_4$ work separately on their specific potential level. The solid solution series $LiMn_yFe_{1-y}PO_4$ turned out to be a promising approach [9–13,20].

* Corresponding author. Present address: Lise Meitner Straße 24, D-89081 Ulm, Germany. Tel.: +49 (0)7319530583; fax: +49 (0)7319530599.
E-mail addresses: michaela.memm@zsw-bw.de (M. Memm), melanie.koentje@zsw-bw.de (M. Koentje), peter.axmann@zsw-bw.de (P. Axmann), margret.wohlfahrt-mehrens@zsw-bw.de (M. Wohlfahrt-Mehrens).

http://dx.doi.org/10.1016/j.jpowsour.2014.09.065
0378-7753/© 2014 Elsevier B.V. All rights reserved.

The cell voltage directly contributes to the energy density. Compared to $LiMnPO_4$ the cobalt and nickel analogues are activated on higher voltage levels [2], thus providing more energy density. However, cost and toxicity are strong disadvantages. Thus, we followed a new model of activating a second redox step in a manganese based system by introducing redox-inactive metals into the $LiMnPO_4$ structure. If it could be possible to utilise a part of the provided capacity of $LiMnPO_4$ at higher potential levels, it would be possible to combine both advantages: environmental benignity and low cost and higher energy density.

2. Experimental

2.1. Synthesis procedure

A co-precipitation of M^{2+} phosphates (M = Fe, Ni, Mn, Mg) and lithium phosphate has been carried out by adding the aqueous solution of the respective salts dropwise to a substrate of an aqueous $Li_xH_{3-x}PO_4$ solution while supervising the percentage of solid matter, stirring speed and pH value. The precipitate was filtered, washed and soaked with an aqueous solution of lactose monohydrate, which would leave a carbon coating on the grains after annealing. All compounds have been treated under nitrogen atmosphere and/or vacuum to exclude oxygen and to avoid the oxidation of Fe^{2+} to Fe^{3+}. The precursor was dried and annealed for 12 h at 725 °C under argon flow. This procedure already has been published by Arnold et al. [17]. For chemical analysis we applied the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP spectroscopy).

2.2. Structural and morphological characterization

XRD measurements have been carried out with a Siemens D5000 diffractometer while Cu Kα radiation was applied. To determine structural parameters, the diffraction profiles were analyzed with quantitative Rietveld refinement using the program TOPAS 2.1 from Bruker AXS. For the main phase the lattice parameters, the crystallite size, the atomic sites and the scale factor have been refined. The space group setting was the orthorhombic space group *Pnma*. Lithium-ortho-phosphate Li_3PO_4 was an intended impurity phase in every sample, since it has been proven, that a small excess of this component avoids Fe^{2+} occupation of Li sites during synthesis that can entail decreased Li ion diffusion along the one dimensional Li diffusion pathways [32]. Integral breadth based volume weighted mean column heights calculation assuming intermediate crystallite size broadening modelled by a Voigt function (LVol-IB) was applied for the evaluation of the crystallite size of the main phase with quantitative Rietveld refinement.

2.3. Electrochemical characterization

The material has been characterized electrochemically in half cells with 3-electrode assembly. The electrode material was composed of 60 wt-% active material, 20 wt-% PTFE-binder and 20 wt-% carbon black. After mixing all components intensely in an agate mortar, flakes of about 50 mg were pressed into a bag-shaped aluminium grid with a pressure of 10 t. The electrode was dried for 12 h in a vacuum oven at 120 °C and then attached to the electrode holder as working electrode vs. lithium metal stripes as counter and reference electrodes. The electrode was electrochemically characterized in 1 M $LiPF_6$, EC:DMC = 1:1 (UBE) with excess electrolyte. CCCV was applied at room temperature with a current rate of *C*/20 and a voltage range between 3.0 V and 5.3 V vs. Li/Li^+. Cell assembly and electrochemical measurements were taken out in an argon glove box.

For the ICP analysis of the charged electrodes the material $LiMg_{0.1}Mn_{0.9}PO_4$ has been converted to an NMP based slurry with the composition active material:carbon black:graphite:PVdF binder = 85:5:5:5. The slurry was casted onto Alumina foil (Korff) before drying at 60 °C over night. The so prepared electrode foil was thoroughly dried at 130 °C in vacuum, before assembling it as a cathode in pouch half cells with Li as counter and reference electrode. 1 M $LiPF_6$ in EC/EMC = 3/7 with 2% VC served as an electrolyte. One of the assembled pouch cells was stored uncycled as a "green" sample during the electrochemical treatment of the others, afterwards all cells were disassembled, washed and their cathodes were subjected to ICP analysis. The "green" cell delivered a basic value of the amounts of Li and P, since the conductive salt cannot be removed completely. An additional ICP analysis of the pure active material revealed the original contents of structurally bound elements. The deviation between both ensures a rough estimation of the error resulting from the electrolyte's conductive salt, which could not be removed by washing. The electrochemical measurement benchmarks were identical with the above described, except the application of a current rate of *C*/25 instead of *C*/50.

3. Results and discussion

To maintain charge balance, equivalent amounts of lithium ions and electrons are exchanged during electrochemical conversion. This coupling limits the redox process in $LiMPO_4$ to the M^{2+}/M^{3+} step [4,9,20]. To activate a second redox step M^{3+}/M^{4+}, residual lithium has to be available in the structure. For $LiMnPO_4$ this can be achieved by partial substitution of Mn^{2+} for electrochemical inactive bivalent ions like Mg^{2+}. Mg^{2+} does not take part at the electrochemical process thus fixing an equivalent of lithium in the host structure which is not removed during the M^{2+}/M^{3+} step (Formula (b)):

Table 1
ICP-analysis and stoichiometry of the phospho-olivine.

Sample	Mixture type	Overall composition from ICP analysis					Stoichiometry $LiMg_xMn_yFe_{1-x-y}PO_4$		
		Li [wt-%]	Mg [wt-%]	Mn [wt-%]	Fe [wt-%]	PO_4 [wt-%]	Mg	Mn	Fe
							x	*y*	1−*x*−*y*
A	Fe	4.61	–	–	34.91	61.00	–	–	1.00
B	Mn	4.87	–	33.02	–	62.05	–	1.00	–
C	Fe–Mg	4.99	4.17	–	25.88	62.23	0.27	–	0.73
D	Mn–Mg	6.26	1.63	26.06	–	64.42	0.12	0.88	–
E	Mn–Mg–Fe	5.70	0.95	25.32	3.09	62.99	0.07	0.83	0.10
F	Mn–Mg–Fe	5.93	2.97	12.44	12.18	65.66	0.22	0.40	0.38
G	Mn–Mg–Fe	6.42	5.18	9.67	9.47	67.25	0.38	0.32	0.30
H	Mn–Mg–Fe	7.95	8.35	5.66	5.28	71.17	0.64	0.19	0.17

Download English Version:

https://daneshyari.com/en/article/1292931

Download Persian Version:

https://daneshyari.com/article/1292931

Daneshyari.com