Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary Information

Experimental Details

Chemicals. Iron(II) acetate (99.995 %), manganese(II) acetylacetonate, lithium ethoxide (95%), LiCl (99.95%), and H_3PO_4 (99.9+%) are used as precursors and anhydrous benzyl alcohol (99.8 %) as solvent. All the chemicals were purchased from Sigma-Aldrich and used as received.

Synthesis. The reaction solutions were prepared under Ar atmosphere in a glovebox and then transferred into a 10 ml microwave glass tube equipped with a Teflon cap. 1 mmol Fe(II) acetate and 1 mmol of LiCl were dissolved in 5 ml benzyl alcohol. After complete dissolution 1 mmol H_3PO_4 is added. Analogously, the $LiMnPO_4$ precursor solution was prepared by mixing Mn(II) acetylacetonate, a slight excess of 1.1 mmol of lithium ethoxide and 1 mmol H_3PO_4 in 5 ml benzyl alcohol. The glass tubes were sealed, taken out of the glovebox and heated at 180 °C for 3 min (also see below). After the thermal treatment the precipitate was extracted by centrifugation and each sample was washed with ethanol and diethyl ether. The solid samples were dried in a lab furnace at 60 °C overnight and finally ground in a mortar to a fine powder.

Microwave heating protocol. The microwave experiments were conducted using a CEM Discover reactor operating at a frequency of 2.45 GHz. The basic configuration of the CEM microwave furnace system consists of a microwave source (magnetron), control device, and a single mode resonant cavity. The cavity is equipped with a variable speed magnetic stirring mechanism and an IR temperature sensor. The power is modulated in function of the temperature and has a maximum operating power of 300 W. A compressed air cooling allows the fast cooling of the sample. In cases where the precursors do not dissolve properly at room temperature, the power is adjusted to heat the sample up to 50 °C, and then the temperature is kept for one minute with vigorous stirring. The organic reaction is induced by increasing the power to 300 W and rapidly heating the solution to 180 °C. Once the temperature is reached, it is kept for 3 min. and then quenched by a compressed air flow.

Characterization. X-ray powder diffraction studies were performed on a Philips PW 1800 diffractometer in reflection mode using a Cu Kα radiation and equipped with a post-sample monochromator. The XRD data were refined by the Rietveld method using the FULLPROF program. Transmission electron microscopy (TEM) as well as high-resolution transmission electron microscopy (HRTEM) characterization was performed on a CM30ST microscope (Philips; LaB_6 cathode, operated at 300 kV, point resolution of 2 Å). For TEM characterization, the wet sample re-dispersed in ethanol after the washing procedure was thoroughly sonicated. One drop of this suspension was placed on a 400-mesh carbon-coated copper grid deposited on a filter paper and left in air to dry. Scanning electron microcopy (SEM) was performed on a LEO 1530 Gemini microscope.

Electrochemical protocol. The electrochemical measurements (cycling and power protocol) were performed at a constant specific current of 0.5–16 C. For the rate capability experiments, the electrodes were cycled galvanostatically in the range of 2.0–4.5 V vs. Li/Li^+ for varying specific currents proportional to the mass of $LiFePO_4$ and $LiMnPO_4$, respectively. In order to promote complete discharge/charge at the respective potential limits, a potentiostatic step was included until the specific current decreased to 34 A kg^{-1}. Dry powder of $LiFePO_4$ and $LiMnPO_4$ was used as the active material. Carbon black (CB, Super P, TIMCAL SA) with a specific surface area of 62 m^2 g^{-1} was used as an electrically conductive additive. Polyvinylidene fluoride (PVDF SOLEF 1015, Solvay) dissolved in N-methylpyrrolidinone (NMP, Fluka) was used as a binder. The proportion of the materials in the electrodes equaled to 83:8.5:8.5 by mass after drying. To prepare the suspensions, all electrode constituents were mixed in NMP with an ultra-sonic stirrer (Hielscher UP 200H, Teltow, Germany) for 1 minute at full power. To prepare test electrodes, all suspensions were doctor-bladed at a "wet" thickness of 250 μm onto aluminum current collector and dried under vacuum at 110 °C overnight. Afterwards, circular working electrodes with a diameter of 13 mm were punched out and dried under vacuum at 120 °C overnight. Coin-type test cells were assembled in an argon-filled glovebox with contents of less than 1 ppm of oxygen, nitrogen, and water. Lithium metal (99.9 %, Aldrich) served as both reference and counter electrode. A fiber glass separator (1 mm thick) was soaked with 500 μl of electrolyte [1 M $LiPF_6$ in ethylene carbonate (EC) / dimethyl carbonate (DMC), 1:1 by mass, Ferro Corp.]. The electrochemical experiments were performed at 25 (± 0.1) °C using standard electrochemical instrumentation.

Table S1. Calculated lattice parameters for the different lithium metal phosphates.

Sample	**$LiFePO_4$**	**$LiMnPO_4$**	**$LiMn_{0.65}Fe_{0.35}PO_4$**
Space group	Pnma	Pnma	Pnma
a (Å)	10.3175	10.4632	10.4155
b (Å)	5.9935	6.1074	6.0691
c (Å)	4.7016	4.7507	4.7322
Volume of the unit (Å^3)	290.743	303.589	299.15
Crystal size (nm)	67.35	263.67	55.27
R_{wp}	9.5	10	10.6
χ^2	4.9	6.9	2.7

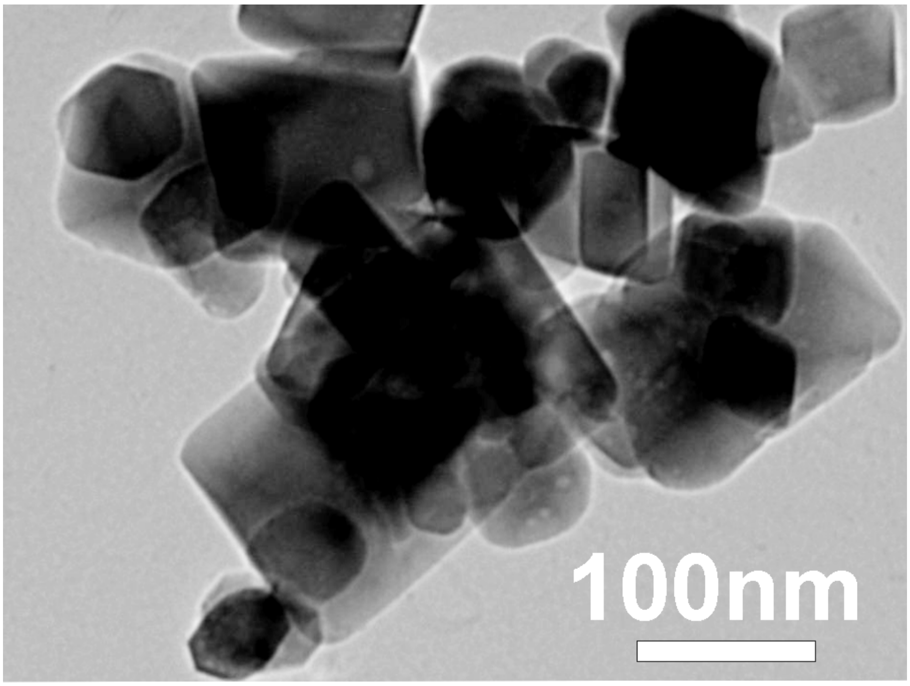

Figure S1. TEM image of $LiMn_{0.65}Fe_{0.35}PO_4$ particles.

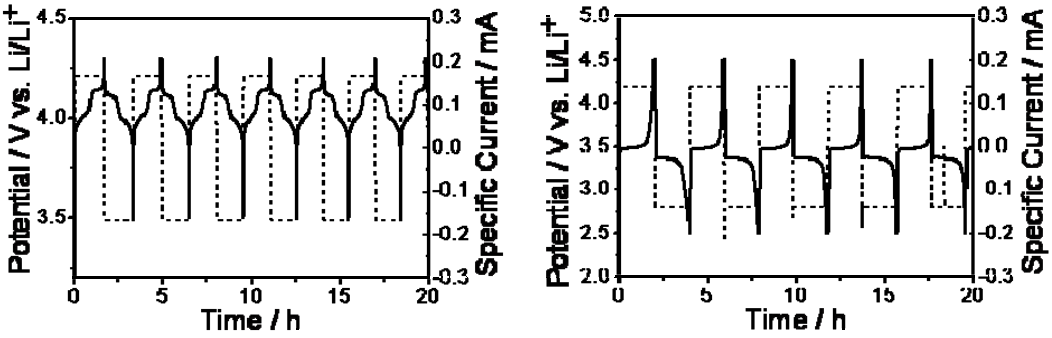

Figure S2. Voltage profiles of $LiFePO_4$ with respect to different voltage regions (4.0–4.5 V and 3.0–3.5 V).

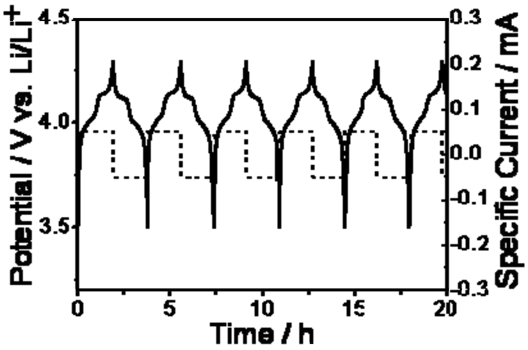

Figure S3. Voltage profile of $LiMnPO_4$.