High voltage Li-ion cell development based on aqueous processing of mixed manganese phosphate cathode and stable electrolytes

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The development of highly efficient batteries is a critical need in automotive industry in order to enable the future success of Electric Vehicles (EV). Active material with higher insertion potential in association with a compliant electrolyte play a very important role for increasing Li-ion cell energy density and, as a consequence, EV autonomy. Moreover, green process like water-based slurries for positive electrode manufacturing allows significant reduction of environmental impact and cost. This work, enclosed in the European SPICY project, presents results for mixed manganese and iron phosphate, $LiFe_{1-x}Mn_xPO_4$ (LFMP), polyanionic cathode with waterborne binders and electrolyte systems stable at high voltage, aiming to develop safe cells with 20% increase in energy density and 20% cost reduction from the $LiFePO_4$ (LFP) baseline.

Polymer binders classically used on the negative electrode, such as Styrene Butadiene Rubber (SBR), are not electrochemically stable at the cathode operating voltages (starts to decompose at 4.2 – 4.3 V). Thus the electrochemical stability window of several waterborne polymeric binders has been analyzed by cyclic voltammetry in 3-electrode Swagelok cells: an acrylate-based latex by Zeon® seems to be stable up to 5 V vs Li^+/Li. Several LFMP active materials with Mn content in the range $0.3<x<0.7$ have been thus formulated in aqueous slurries with sodium carboxymethyl cellulose (CMC) and acrylate-based latex binders. Positive electrodes based on LFP and LFMP (89 wt.% active mass) have been prepared showing suitable mechanical properties for high areal loadings up to 2.4 mAh cm^{-2}. Graphite electrodes of 95 wt.% active mass loading and 2.65 mAh cm^{-2} (water-based CMC/SBR formulation) have been used in full coin cells to assess electrochemical performance with different additives (VC, FEC, LiTFSI), carbonates and new solvent-based (sulfolane, SL and adiponitrile, ADN) electrolytes. Best performing cathode has been achieved for the active material composition $LiFe_{0.45}Mn_{0.55}PO_4$ (155 mAh g^{-1}; >600 Wh kg^{-1}). High initial coulombic efficiencies are obtained (83-85%) in full Li-ion cells for several of the studied electrolytes, allowing for 140 mAh $g_{(LFMP)}^{-1}$ at low discharge-rates (C/20) and ca. 115 mAh $g_{(LFMP)}^{-1}$ at high discharge rate (3C). Cycle-life tests at 1C charge/discharge (100% DoD, voltage window 2.5 – 4.4 V) have shown stable cycling behavior with a delivered capacity of ~120 mAh $g_{(LFMP)}^{-1}$ and capacity retention above 90% after 300 cycles for three electrolytes: 1M $LiPF_6$ EC:DMC:PC +2wt%VC, 1M $LiPF_6$ EC:DMC+2wt%LiTFSI and 1M $LiPF_6$ SL:DMC +2wt%VC. Updated electrochemical data will be provided confiming the feasibility of LFMP/Graphite cells with increased energy density, nominal voltage 3.6 V, good power rate and stable cycle-life.

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