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First report of Pn - $\text{Li}_2\text{MnSiO}_4$ synthesized by ion-exchange

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Since the electrochemical activity of lithium metal silicates was demonstrated by Nyten et al. (1) for $\text{Li}_2\text{FeSiO}_4$, there has been a lot of interest in the silicates family. The Li_2MSiO_4 ($M = \text{Fe}, \text{Mn}, \text{Co}$) family features a high theoretical capacity of 333 mAh g^{-1} if the two lithium ions can be extracted. In particular, $\text{Li}_2\text{MnSiO}_4$ has attracted attention due to its higher voltage and the low toxicity of manganese. Due to the low electronic conductivity, ball-milling and carbon coating are necessary to improve the electrochemical performance. However, the capacity fading is also large due to the amorphization of the material beyond the extraction of one lithium, limiting the capacity to 166 mAh g^{-1} (2). To go around this problem, we took advantage of the rich polymorphism of the silicate family to synthesize a new polymorph that could be potentially more stable in the delithiated form than thermodynamic polymorphs (3). In this work, Na^+ ions were exchanged from $\text{Na}_2\text{MnSiO}_4$, which adopts the Pn structure and $\text{Li}_2\text{MnSiO}_4$ and LiNaMnSiO_4 were obtained by controlling the ion-exchange conditions. Materials were characterized by SEM and TEM and their electrochemical performance were assessed by electrochemical cycling and compared to the thermodynamic polymorph of $\text{Li}_2\text{MnSiO}_4$. Density-functional theory (DFT) calculations were carried out to determine the lattice parameter, atomic coordinates, lithium extraction voltage and stability of the polymorphs.

$\text{Na}_2\text{MnSiO}_4$ was synthesized from a sol-gel method and the Na^+ ion were exchanged for Li^+ by either refluxing with an excess of LiBr in hexanol or hydrothermally with an excess of LiBr . The electrochemical testing was done in 2325-type coin cells with lithium anode, Celgard separators and 1M LiPF_6 in EC:DEC (3:7) between 1.8 V and an upper voltage between the range of 4.4V to 4.6V.

The structure of Pn - $\text{Li}_2\text{MnSiO}_4$ vs. the thermodynamic $Pmn2_1$ is shown in Figure 1. The delithiated form of the $Pmn2_1$ polymorph is layered, while the Pn one is a framework which could indicate better stability. Rietveld analysis of XRD pattern using refined lattice parameter and atomic coordinates fixed at values obtained from DFT calculations were able to confirm that Pn - LiNaMnSiO_4 and Pn - $\text{Li}_2\text{MnSiO}_4$ structures were obtained from the ion-exchange. Coexistence of spherical and needle-shaped particles, deduced by analysis of the XRD pattern, was confirmed by TEM measurements. Electrochemical measurements shown in Figure 2 show that both Pn and $Pmn2_1$ polymorphs of $\text{Li}_2\text{MnSiO}_4$ yield the same capacity (110 mAh g^{-1} initially) and both experience capacity fading while Pn - LiNaMnSiO_4 yields a lower (50 mAh g^{-1}) but stable capacity. Li^+ can also be exchanged in-situ by cycling $\text{Na}_2\text{MnSiO}_4$ directly as a cathode material. A

gradual exchange of Na^+ ions occurs and the capacity increases from 20 mAh g^{-1} to 60 mAh g^{-1} . The thermal stability of the polymorphs was investigated by DSC and will also be discussed.

Figure 1. XRD patterns of ZnMn_2O_4 powders sintered at 400°C , 600°C , 800°C , and 1000°C .

Figure 2. Discharge capacities of $\text{Li}_2\text{MnSiO}_4$ Pn , $\text{Li}_2\text{MnSiO}_4$ $Pmn2_1$, LiNaMnSiO_4 Pn and $\text{Na}_2\text{MnSiO}_4$ Pn .

References

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