Solid-State ^{6}Li NMR Characterization of Lithium-Metal Orthosilicate Materials for Applications in Lithium Ion Batteries

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Introduction

Lithium metal orthosilicates (Li_2MSiO_4, M=Fe, Mn, Co) are a class of "polyanion" compounds containing compact tetrahedral "anion" structural units $(SiO_4)^{4-}$ with strong covalent bonding for lithium-ion batteries. Over the most widely used lithiated metal oxide materials (e.g. $LiCoO_2$), lithium metal orthosilicate materials exhibit significant advantages with potentially low cost, non-toxicity, and highly thermal stability (*1*). However, their electronic conductivity and lithium-ion diffusion rate are relatively low, which could be intrinsic for polyanion compounds. Various material processing approaches including the use of carbon coatings, mechanical grinding or mixing, cation doping, etc. have been used to improve the conductivity of the silicate-based materials. Here, we use high-resolution ^{6}Li solid-state NMR to characterize the lithium ions and their dynamics in lithium manganese orthosilicate materials, thus to ultimately provide a guideline for improving the performance of the polyanion compounds for lithium ion batteries.

Experimental

High-resolution ^{6}Li solid-state NMR experiments were carried out on a Bruker DMX 300 NMR spectrometer using Bruker 4.0mm HX MAS probe at the NHMFL.

Results and Discussion

Fig.1 shows the ^{6}Li MAS NMR spectra of Li_2MnSiO_4 and lithium-rich $Li_{2.6}Mn_{0.7}SiO_4$. The ^{6}Li resonances are positioned at 0.5, -112, and -134 ppm. The peak at 0.5 ppm is very narrow representing the Li-ions that participate in ion conductivity, while the peaks at -112 and -134 ppm are associated with the localized Li ions. The two localized ^{6}Li resonances imply the existence of two types of frame structures in the polyanion compound. For Li_2MnSiO_4 material, out of the two electrons per transition metal Mn, only about 0.7 electrons are available for ion exchange, although carbon coatings could increase the number of electrons available for ion exchange to 1.3 (*1*). Most likely, those localized Li-ions form covalent bonds with the frame structural units so strongly that they can hardly be available for ion exchange. As shown in Fig.1B, the lithium-rich $Li_{2.6}Mn_{0.7}SiO_4$ significantly increases the Li-ions available for ion conductivity, while it has little effect on the frame structural units. Thus, the lithium-rich $Li_{2.6}Mn_{0.7}SiO_4$ has much better performance than the Li_2MnSiO_4, as expected (unpublished results). Fig.2 shows the inversion recovery of the ^{6}Li signals of the lithium-rich $Li_{2.6}Mn_{0.7}SiO_4$. For the signal at 0.5 ppm, the fitting yielded two T_1 components (0.037 and 1.26 s). While for the signals at -112 and -134 ppm, the magnetization apparently overshoots to a maximum above the equilibrium value and then slowly decays back to the equilibrium at a time constant of ~1.26 s, which is the same as the slow relaxation component for the signal at 0.5 ppm. Such phenomena (*2*) indicate that there exist effective couplings (i.e., cross relaxation) between the exchangeable ions and those localized ions that could greatly facilitate the lithium-ion intercalation and lithium-ion diffusion (*3*).

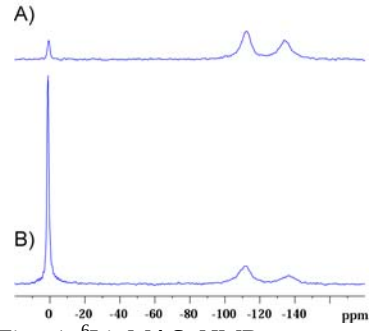

Fig. 1 ^{6}Li MAS NMR spectra of Li_2MnSiO_4 (A) and $Li_{2.6}Mn_{0.7}SiO_4$ (B). The ^{6}Li chemical shift was referenced to the ^{6}Li signal of LiCl.

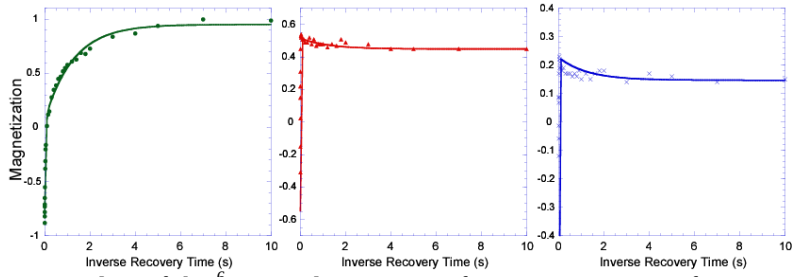

Fig. 2. Plots of the ^{6}Li signal intensities of $Li_{2.6}Mn_{0.7}SiO_4$ as a function of inverse recovery time. Green, Red, and Blue are used to represent the signals at 0.5, -112, and -134 ppm, respectively.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (29925310 and 20473060) and the National Basic Research Program of China (973 Program, Grant# 2007CB209702). ^{6}Li NMR experiments were performed at the NHMFL.

References

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