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Synthesis of Co-free and Li-excess positive electrode materials for lithium-ion battery

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Co-free positive electrode material is necessary as constituent material for large-scale lithium-ion battery to use electronic vehicle (EV) and plug-in hybrid one (PHEV). As shown in Figure 1, we developed seven high-capacity material systems (>200 mAh/g) having above 3.2 V of discharge voltages. Our main strategy was utilizing Fe ion for oxide-based positive electrode material, because iron is cheap and environmental-friendly element and $LiFeO_2$ is known as an electrochemically-inactive positive electrode material. To activate the $LiFeO_2$ component, we have been trying to make novel $LiFeO_2$-Li_2MnO_3 solid solution (FM system). The first paper was published in 2001 and the study is still going on to improve its electrochemical property. To synthesize homogeneous FM sample with high Fe content, careful optimization of preparation condition must be needed. Original co-precipitation–calcination method was constructed. The co-precipitation temperature was kept to low temperature (-10°C) to avoid spinel ferrite formation and then it wet-oxidized by bubbling with air. This precursor preparation technique is very important. After washing and mixing with Li salt, the mixture was dried for pulverization. It calcined in air or N2 flow. Other systems were derived from the FM one. Among them, the $LiFe_{1/2}Ni_{1/2}O_2$-Li_2MnO_3 solid solution (FNM system) was designed to raise discharge voltage close to 3.5 V. Applying stepwise-charging method, its electrochemical properties was rather improved. $LiFeO_2$-Li_2MnO_3-Li_2TiO_3 (FMT system) and Li_2TiO_3-Li_2MnO_3 (TM system) solid solutions were synthesized by co-precipitation–calcination-carbothermal reduction process. NiO-Li_2MnO3 (NM system) and NiO-Li_2MnO_3-Li_2TiO_3 (NMT system) was prepared by co-precipitation–hydrothermal–calcination process. The LN system was considered as Li-excess $LiNiO_2$ which was synthesized by thermal decomposition of Li_2NiO_3. Research details for these selected systems will be presented.

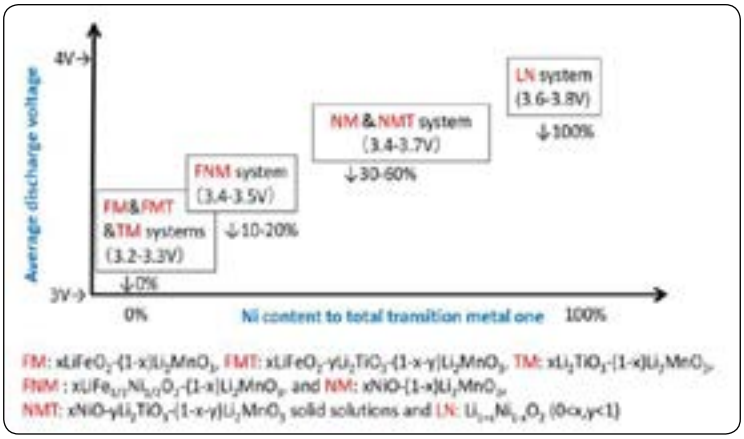

Figure 1: Our developed positive electrode materials vs. their average discharge voltages

Recent Publications

1. M Tabuchi, H Kageyama, H Shibuya, K Doumae, R Yuge and N Tamura (2016) Stepwise charging and calcination atmosphere effects for iron and nickel substituted lithium manganese oxide positive electrode material. Journal of Power Sources 313:120–127.
2. M Tabuchi, H Kageyama, K Takamori, Y Imanari and K Nakane (2016) Synthesis and electrochemical characterization of Ni- and Ti-substituted Li_2MnO_3 positive electrode material using co-precipitation–hydrothermal–calcination method. Electrochmica Acta 210:105–110.
3. M Tabuchi, N Kuriyama, K Takamori, Y Imanari and K Nakane (2016) Appearance of lithium-excess $LiNiO_2$ with high cyclability synthesized by thermal decomposition route from $LiNiO_2$-Li_2NiO_3 solid solution. J. Elecrtochem. Soc. 163(10):A2312–A23.
4. M Tabuchi, Y Nabeshima, T Takeuchi, H Kageyama, J Imaizumi, H Shibuya and J Akimoto (2013) Synthesis of high-capacity Ti- and/or Fe-substituted Li_2MnO_3 positive electrode materials with high initial cycle efficiency by application of the carbothermal reduction method. Journal of Power Sources 221:427–434.
5. M Tabuchi, Y Nabeshima, T Takeuchi, K Tatsumi, J Imaizumi and Y Nitta (2010) Fe content effects on electrochemical properties of Fe-substituted Li_2MnO_3 positive electrode material. Journal of Power Sources 195(3):834–844.

Biography

Mitsuharu Tabuchi is a solid-state Chemist, developing novel positive electrode materials for lithium-ion battery. He developed an original synthetic route to accomplish a complete mixing of two or three kinds of transition metal ions at AIST. He is also skilled in Rietveld x-ray analysis and ^{57}Fe Mössbauer spectroscopy for material characterization.

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