Abstract #870, 224th ECS Meeting, © 2013 The Electrochemical Society

Novel fluorophosphate-based cathode materials for Li- and Na-ion batteries

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Recently, we have reported a novel layered lithium vanadium fluorophosphate, $Li_{1.1}Na_{0.4}VPO_{4.8}F_{0.7}$, as a promising cathode material for Li-ion batteries.[1] Starting from $Na_{1.5}V^{4+}PO_5F_{0.5}$, we tried to reduce the initial vanadium oxidation state by controlling the degree of fluorination (δ) in $Na_{1.5}VPO_{5-\delta}F_{0.5+\delta}$. By changing the stoichiometric ratio of precursors, we could synthesize a pure-phase $Na_{1.5}VPO_{4.8}F_{0.7}$. The lattice parameter change for $Na_{1.5}VPO_{5-\delta}F_{0.5+\delta}$ samples having different degrees of fluorination was continuous, implying the solid-solution behavior. By the double titration method, we found that the oxidation state of vanadium of $Na_{1.5}VPO_{4.8}F_{0.7}$ (δ = 0.2) was *ca*. +3.8. This means that we can utilize the extended redox range of vanadium ($V^{3.8+}/V^{5+}$) allowing a multi-electron redox reaction. Also, we could tune the oxidation state of vanadium by controlling the degree of fluorination.

In fact, in the new lithium phase, $Li_{1.1}Na_{0.4}VPO_{4.8}F_{0.7}$, which was synthesized *via* Na^+/Li^+ ion-exchange from $Na_{1.5}VPO_{4.8}F_{0.7}$, more than one electron participated in the electrochemical reaction. About 1.1 Li^+ ions could be reversibly released and reinserted *via* the multi-electron redox couple of $V^{3.8+}/V^{5+}$ (1.2 e^- transfer). The resulting capacity was *ca*. 157 mAh g^{-1} (*see* Figure 1) which far exceeded the capacity of $Li_{1.1}Na_{0.4}V^{3.8+}PO_{4.8}F_{0.7}$, 143 mAh g^{-1} (based on 1 e^- transfer). The average voltage was *ca*. 4 V (*vs*. Li^+/Li), and the resulting energy density was 624 Wh kg^{-1}. This value is higher than that of $LiFePO_4$ (~590 Wh kg^{-1}), which is one of the most promising cathode materials for Li-ion batteries.

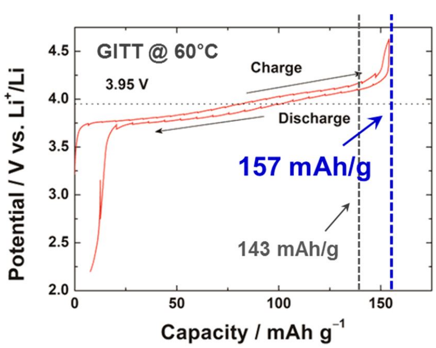

Figure 1. Galvanostatic intermittent titration technique (GITT) curve for $Li_{1.1}Na_{0.4}VPO_{4.8}F_{0.7}$ electrode at 60°C.

Furthermore, excellent capacity retentions of 98% and 96% after 100 cycles were obtained at 60°C and room temperature, respectively. This could be explained by exceptionally small volume change during cycling and the rigid polyanion framework. The cell volume difference between the pristine and fully charged phase was only 0.7%. This value is comparable to that of recently reported triplite $Li(Fe_{1-\delta}Mn_{\delta})SO_4F$.[2]

Unexpectedly high rate capability was delivered for both charge/discharge despite the micron-sized particles, which promises further enhancement of power density by nanosizing. This fast kinetics may originate from the structural merits of $Li_{1.1}Na_{0.4}VPO_{4.8}F_{0.7}$. Both the open structure and the two-dimensional diffusional pathways (*see* Figure 2) allowed the fast motion of Li^+ ions.

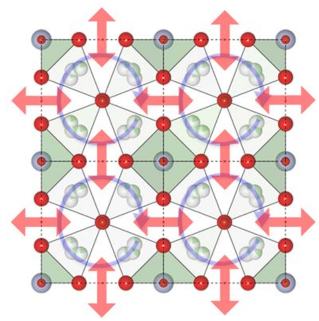

Figure 2. Two-dimensional diffusional pathways for Li hopping in the crystal structure of $Li_{1.1}Na_{0.4}VPO_{4.8}F_{0.7}$.

$Na_{1.5}VPO_5F_{0.5}$ and $Na_{1.5}VPO_{4.8}F_{0.7}$ are not limited to the starting materials to prepare the new lithium phase. Rather, they can be good cathode materials for Na-ion batteries. In effect, studies on the $Na_{1.5}VPO_5F_{0.5}$ cathode have been steadily reported.[3,4]

The fluorinated new sodium phase, $Na_{1.5}VPO_{4.8}F_{0.7}$, can be a promising cathode for Na-ion batteries because it allows the multi-electron transfer (1.2 e^-) beneficial to the energy density. According to our preliminary data, it shows one of the smallest volume changes upon cycling (*ca*. 2%) among cathode materials for Na-ion batteries. This promises excellent cycle life, which is under test. Furthermore, in-depth study on the charge/discharge mechanism of $Na_{1.5}VPO_{4.8}F_{0.7}$ cathode by the combined first-principles and experiments is in progress.

References

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