Charge-discharge performance of amorphous $Na_{0.7}CoO_2$-Na_xMO_y positive electrode active materials in bulk-type all-solid-state sodium batteries

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All-solid-state sodium batteries with high safety and reliability are promising as next generation batteries. We have reported that the all-solid-state sodium cell ($Na_{15}Sn_4$/Na_3PS_4 glass-ceramic/crystalline TiS_2) worked as a secondary battery, showing the reversible capacity of *ca.*100 mAh g^{-1} and the avarage discharge potential of 1.4 V[1]. To achieve higher energy density, discovery of a novel positive electrode active material with high capacity and high operation voltage is desired. The layered transition metal oxides with high operation voltage have been studied as representative active materials. Recently, we have proposed the amorphization of lithium transition metal oxide with lithium oxy-acids such as $LiCoO_2$-Li_2SO_4 system by a mechanochemical technique[2]. The all-solid-state cell using only the amorphous $80LiCoO_2 \cdot 20Li_2SO_4$ (mol%) active material in a positive electrode layer worked as a secondary battery and showed a large capacity of 163 mAh g^{-1} at 100ºC. The electrochemical performances of $LiCoO_2$ was improved by amorphization with Li_2SO_4. $Na_{0.7}CoO_2$ is a well known layered transition metal oxide as an active material in the sodium-ion system[3]. In this study, the amorphous positive electrode active materials composed of $Na_{0.7}CoO_2$ and sodium oxy-acids were prepared for all-solid-state sodium batteries.

Amorphous $Na_{0.7}CoO_2$-Na_xMO_y (M=N, S, P, B, and C) positive electrode active materials were synthesized by a mechanochemical technique. XRD patterns of the samples showed no diffraction peaks attributable to starting materials, indicating that the reactions between $Na_{0.7}CoO_2$ and Na_xMO_y proceeded. The $80Na_{0.7}CoO_2 \cdot 20NaNO_3$ (mol%) ($Na_{0.76}Co_{0.8}N_{0.2}O_{2.2}$) had high formability to be densified just by pressing at room temperature. Bulk-type all solid-state sodium cells ($Na_{15}Sn_4$/Na_3PS_4 glass-ceramic/$Na_{0.7}CoO_2$-Na_xMO_y) were fabricated and their electrochemical properties were investigated. The cell using the $Na_{0.76}Co_{0.8}N_{0.2}O_{2.2}$ active material without any conductive additives as a positive electrode layer (*ca.* 50 μm thickness) operated as a secondary battery at 25ºC; an average discharge potential was 2.9 V and an initial discharge capacity was 70 mAh g^{-1} of positive electrode. The cell showed a higher discharge voltage and a larger capacity than that of the cells using the crystalline $Na_{0.7}CoO_2$ or the milled $Na_{0.7}CoO_2$ without any additives as a positive electrode layer. The electrochemical properties of the $Na_{0.7}CoO_2$ were improved by amorphization with $NaNO_3$. Amorphization of layered transition metal oxides with sodium oxy-acids is an effective way in achieving novel active materials with high capacity.

References:

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