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Insights into charge storage and electroactivation of mixed metal sulfides in alkaline media: NiCoMn ternary metal sulfide nano-needles forming core–shell structures for hybrid energy storage

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Abstract

Mixed metal sulfides have recently attracted great attention for energy storage applications due to their low cost and enhanced electrical/electrochemical performance compared to oxide/hydroxide analogues. Despite of being demonstrated as high performance energy storage electrode materials, a profound understanding of their electrochemical signal is vital to unravel their charge storage mechanism and achieve a roadmap for rational design and engineering of high-performance electrode materials. Herein, energy storage properties of directly grown $Ni_{1.80}Co_{0.50}Mn_{0.50}S_{1.52}$ (NCMS) nano-needles on nickel foam were evaluated as novel binder/additive-free high-performance electrodes in alkaline media and their electro-activation process and charge storage mechanism were tracked through *ex situ* XRD and *operando* Raman spectroscopy. Accordingly, NCMS nano-needles exhibited a high specific capacity of 138 mA h g^{-1} (0.71 mA h cm^{-2}), excellent rate capability and exceptional cycling stability demonstrating a peculiar electro-activation over cycling (the specific capacity increased by almost 2 times ~220 mA h g^{-1}). STEM, *ex situ* XRD and Raman spectroscopy at different states of charge and after cycling suggested the growth of amorphous hydroxide phases at the surface, resulting in the formation of a core–shell structure during cycling. To further confirm this hypothesis charging/discharging process using *operando* Raman spectroscopy was conducted in the mixed metal sulfide electrode. Based on the obtained results, a charge storage mechanism was proposed. In addition, when integrated with rGO electrodes in an asymmetric device, NCMS nano-needles exhibited a maximum energy density of 36.2 W h kg^{-1} and power density of 16.5 kW kg^{-1}, with evidenced long-term cycling and rate performance. Therefore, the present work not only sketches electrochemical behavior of NCMS but also helps to achieve a better understanding of the electro-activation process and charge storage origin of mixed metal sulfides in alkaline media.

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