Metal hexacyanoferrates as cathode materials for Zn-ion batteries

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Transition metal hexacyanoferrates (MeHCF) of general formula $A_xMe_y[Fe(CN)_6]_z \cdot nH_2O$ (A – alkali metal cation, and Me^{2+} = Mn, Fe, Co, Ni, Cu, Zn, etc.) have an open type channel crystal structure with the size of the channel sufficient for reversible intercalation of Zn^{2+} cations. This makes MeHCF promising cathode materials for zinc-ion batteries (ZIBs) [1, 2, 3].

In this work we synthesized potassium-vanadyl hexacyanoferrate (VHCF), copper(II) hexacyanoferrate, potassium-manganese (II) hexacyanoferrate, cobalt (II) hexacyanoferrate, and manganese (II) hexacyanoferrate and compared their electrochemical behavior in 1M aqueous solutions of $ZnSO_4$.

The cyclic voltammetry of all the MeHCFs in zinc sulfate solutions showed at least two cathodic and (or) anodic peaks. The variation of the transition metal (V, Cu, Ni, Co) in the hexacyanoferrate enables the battery voltage adjustment by the redox potential of the corresponding half-reaction that involves different valence states of the d-element.

VHCF is not well described in the literature, though the variety of available vanadium oxidation states may result in considerably high material specific capacity. Thus we studied its electrochemistry in greater detail, using both aqueous and non-aqueous zinc salt electrolytes. The specific capacity of VHCF cathodes reaches 43 mAh/g in 1M aqueous solutions of $Zn(CF_3SO_3)_2$, while the capacity in 1M $Zn(CF_3SO_3)_2$ solution in acetonitrile was found to be only 20 mAh/g which indicates a significant role of protons in the process of charge storage in aqueous VHCF-based ZIB. The cyclability of VHCF in acetonitrile-based electrolyte was found to be better than that in aforementioned aqueous 1M $Zn(CF_3SO_3)_2$ electrolyte. The usage of concentrated zinc salt solution helps to improve cyclability of aqueous VHCF-based ZIB.

References

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