

MS14-1-11 Structure–performance relationships in $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ anodes for Na-ion batteries
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Abstract

Due to the tremendous growth of the electric vehicle industry and demand for Li-ion batteries recently, we may soon face a shortage of these crucial components. At the same time, we observe spiking prices of key elements such as lithium, nickel, cobalt and graphite necessary for battery production [1]. Na-ion technology emerges as an economically promising alternative to Li-ion because of the low price of raw elements (sodium, iron) as well as comparable performance. Though most of the proposed anode materials for Na-ion batteries are based on carbon chemistry, these exhibits very low Columbic efficiency during the first charging/discharging cycle and require a high temperature of pyrolysis. On the other hand elements such as Sn, Sb, Si, and P yield high capacities, but degrade rapidly due to volume changes up to 400%. Here we focus on iron-titanium-based oxide anodes that take employ intercalation mechanism to react with sodium and thus better retain the capacity because of minor changes in crystal structure during (de)sodiation. We prepared NaFeTiO_4 , $\text{Na}_{0.9}\text{Fe}_{0.9}\text{Ti}_{1.1}\text{O}_4$ and $\text{Na}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$ via both citrate-assisted sol-gel methods as well as traditional high-temperature solid-state route and compared the performance in the Na-ion batteries [2]. Crystal structure, chemical composition and morphology were determined using X-ray diffraction (XRD), scanning electron microscopy (SEM) and nitrogen adsorption isotherms. The crystal structure of NaFeTiO_4 possesses single-barreled tunnels occupied by sodium that stand as a pathway for the rapid diffusion of sodium ions. During the synthesis, if the sodium content is reduced below one and some iron ions are replaced for titanium then the single-barreled tunnels become double-barreled and as a consequence, an additional diffusion path can be formed ($\text{Na}_{0.9}\text{Fe}_{0.9}\text{Ti}_{1.1}\text{O}_4$ and $\text{Na}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$). Impedance spectroscopy (IS) measurements in the temperature range of 25 – 300°C confirm that electrical conductivity of $\text{Na}_{0.9}\text{Fe}_{0.9}\text{Ti}_{1.1}\text{O}_4$ and $\text{Na}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$ is one order of magnitude higher than NaFeTiO_4 while the activation energy is lower (0.82 eV vs 0.86 eV) indicating better kinetics of combined sodium and electron migration. At the same time, double-barreled compounds are characterized by lower band-gap values (UV-VIS measurements). Among all of the investigated materials, $\text{Na}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$ has the highest charge capacity of about 180 mAh g⁻¹ during the first cycle at C/20 and can retain 80% of the initial capacity after 30 cycles with an average charging voltage of 1.3 V vs. Na⁺/Na. Ex-situ XRD of the recovered electrode layers after a full discharge as well as a complete discharging-charging cycle indicate minor changes in the volume of the elemental cell. Also, the changes in the local environment of Fe and Ti have been identified in X-ray absorption spectroscopy (XAS). Finally, the capacities exceeding 177 mAh g⁻¹ measured at 60°C indicate that beside the Fe³⁺/Fe²⁺ redox, also Ti⁴⁺/Ti³⁺ may be involved during the sodiation process. We hope that due to the low cost and abundance of raw elements and promising electrochemical performance, $\text{Na}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_4$ may find application as anode material in the future generation of Na-ion batteries. Acknowledgments: This work was supported by the Polish Ministry of Science and Higher Education (MNiSW) under grant number 0046/DIA/2017/46

References

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