

SYNTHESIS OF $\text{Na}_3\text{MnPO}_4\text{CO}_3$ AND $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ AS CATHODE MATERIALS FOR AQUEOUS NA-ION BATTERIES

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Introduction

In order to meet the Paris climate agreement goals of future energy requirements [1], as well as the climate neutrality by 2050 [2], the development of renewable energy sources has become more and more urgent. Although the electricity generated by wind turbines, solar panels or hydropower is clean and safe, the supply is of intermittent nature and requires large-scale storage devices in order to obtain a balance. Electrochemical energy storage has many desirable features such as pollution-free operation, high round-trip efficiency, wide range of power and energy, long cycle life and low maintenance, as well as easy integration into the grid [3]. Various novel materials have been investigated and reported as cathodes and anodes for aqueous sodium-ion batteries, however there are still several problems such poor cycle stability, low energy density or low voltage which should be acknowledged [4]. After all, Mn-based (mixed)phosphate cathodes have a lot of advantages such as widespread availability of raw materials, low cost, high safety and non-toxicity. Moreover, Mn-based framework materials distinguish themselves as good candidates for fast sodium intercalation, small lattice volume changes and high insertion potentials [5].

Results

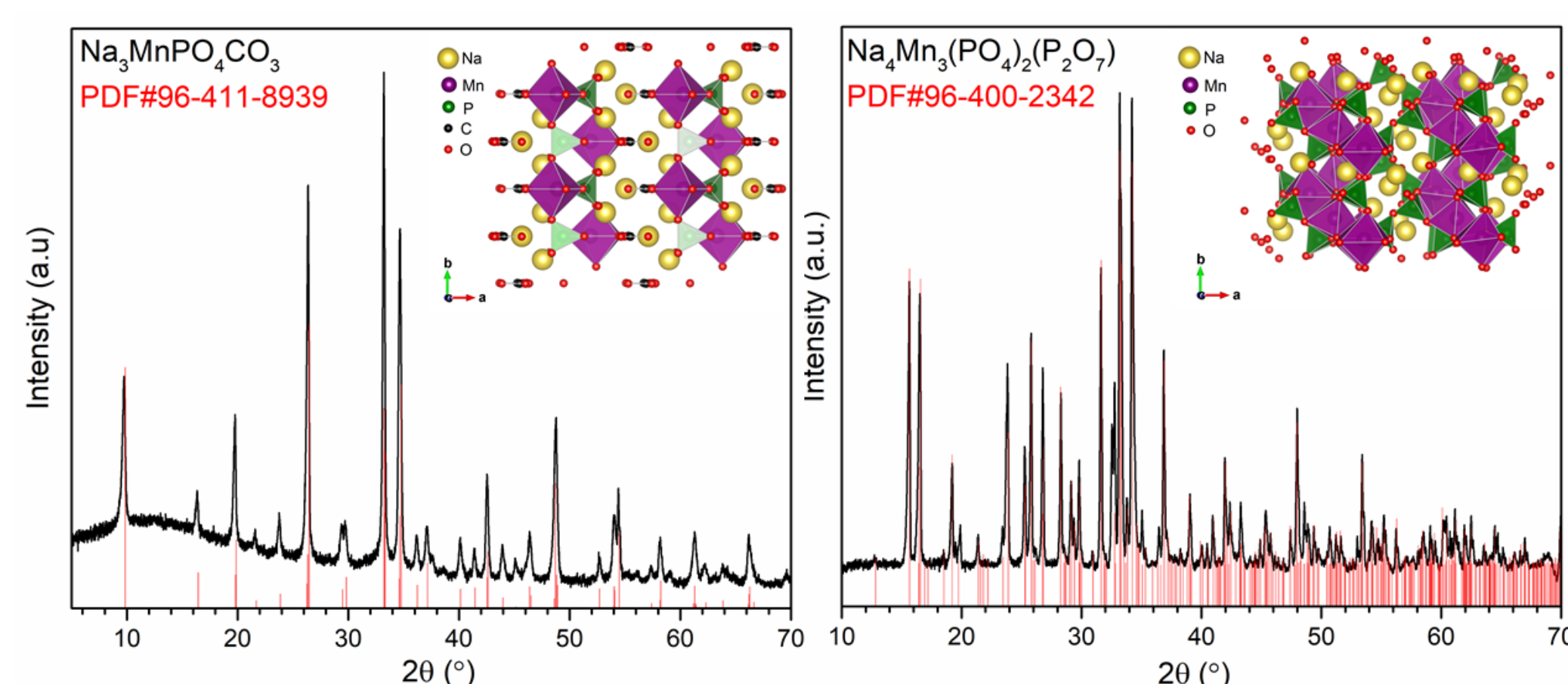


Fig. 2. XRD patterns of $\text{Na}_3\text{MnPO}_4\text{CO}_3$ and $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$

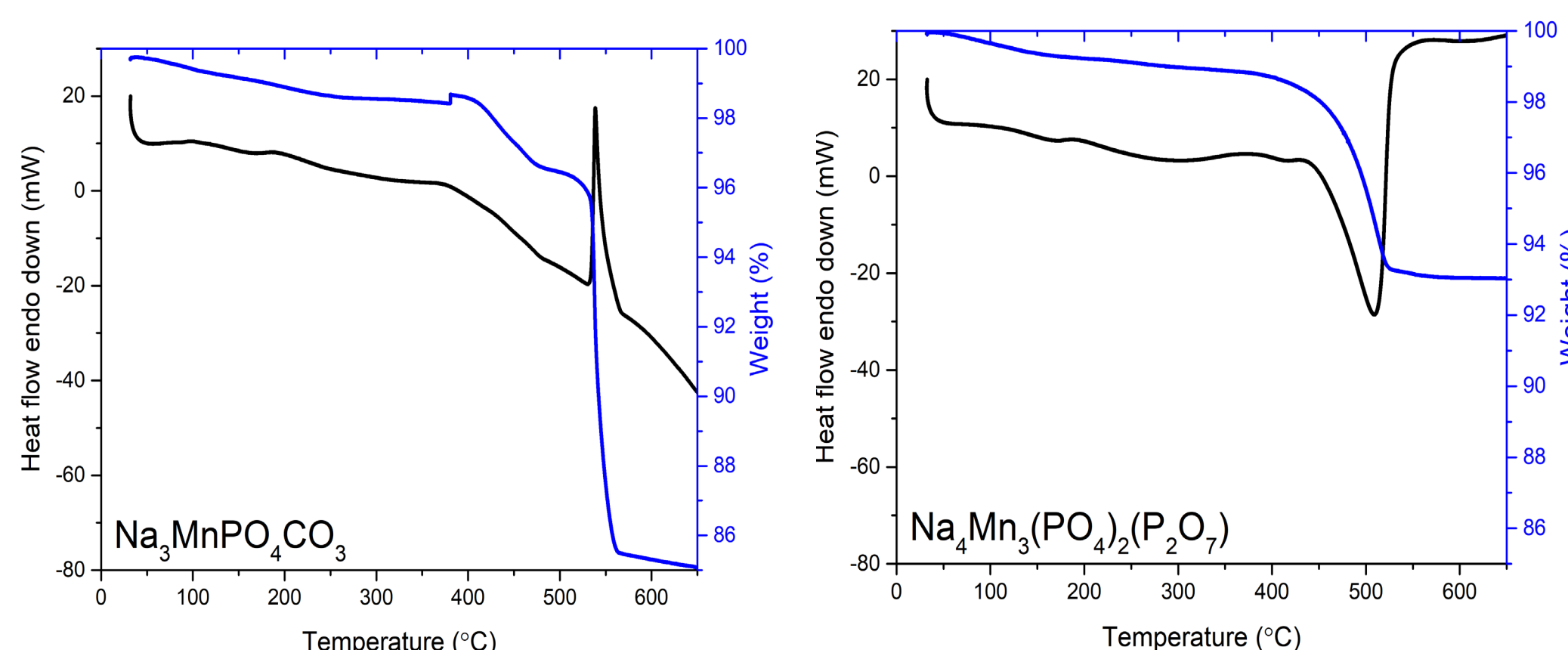


Fig. 2. Thermogravimetric analysis results of $\text{Na}_3\text{MnPO}_4\text{CO}_3$ and $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$

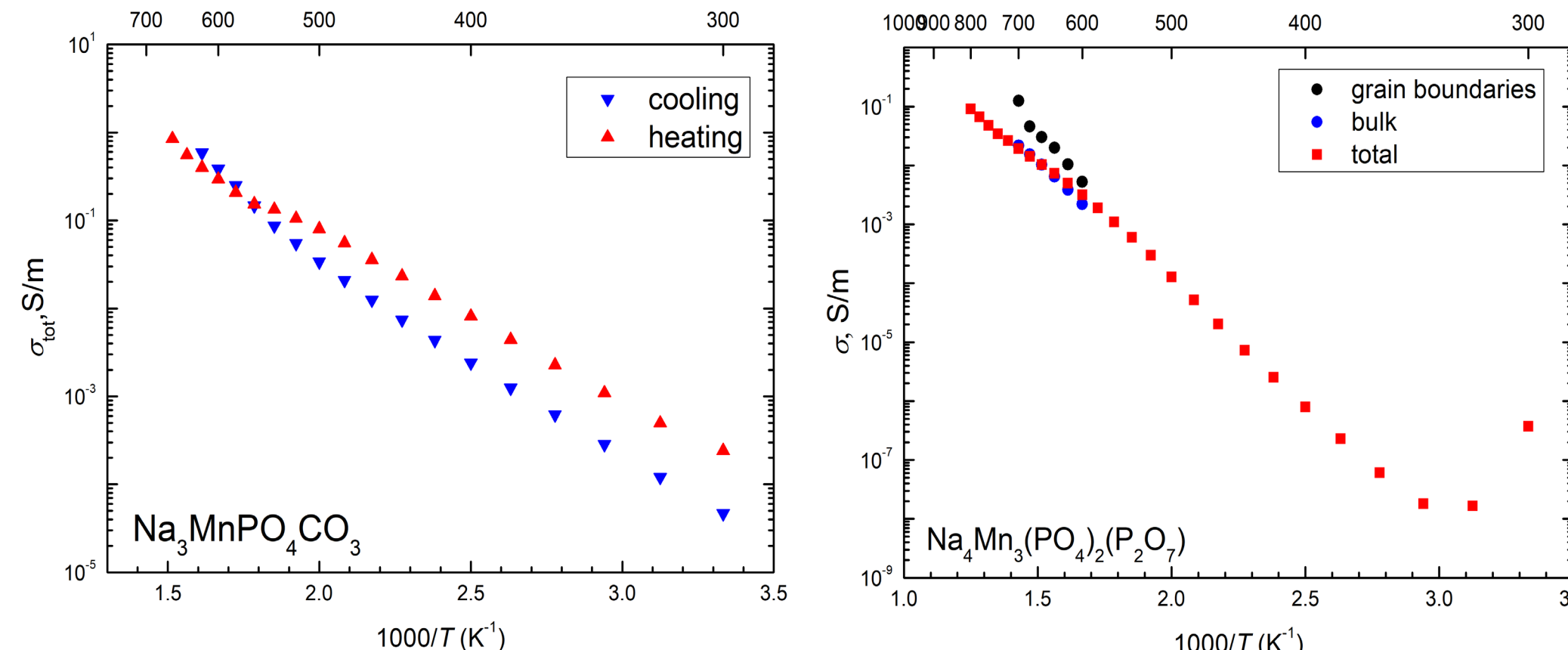


Fig.3. Ionic conductivity results of $\text{Na}_3\text{MnPO}_4\text{CO}_3$ and $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$

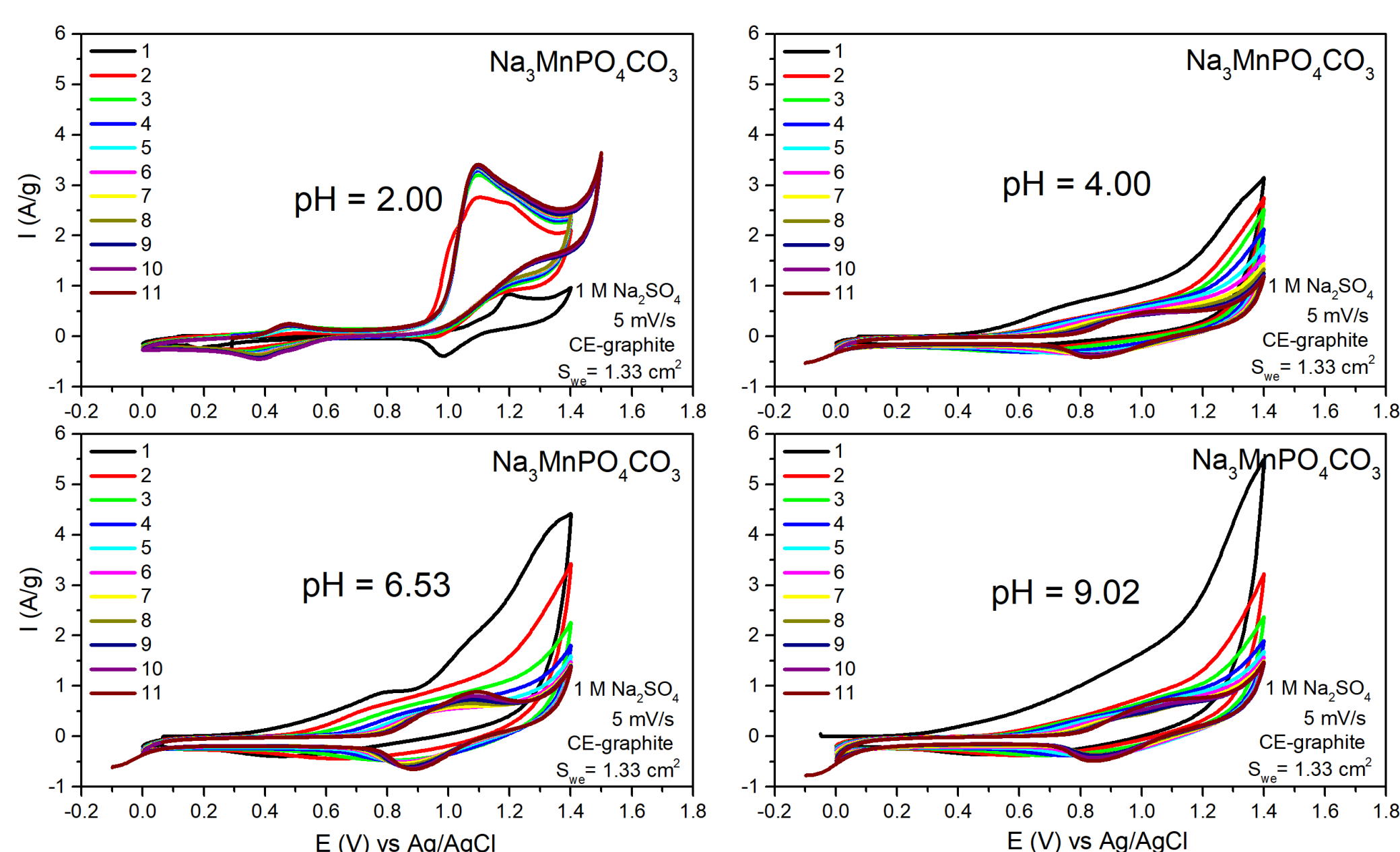


Fig. 4. Cyclic voltammograms of $\text{Na}_3\text{MnPO}_4\text{CO}_3$ at different pH

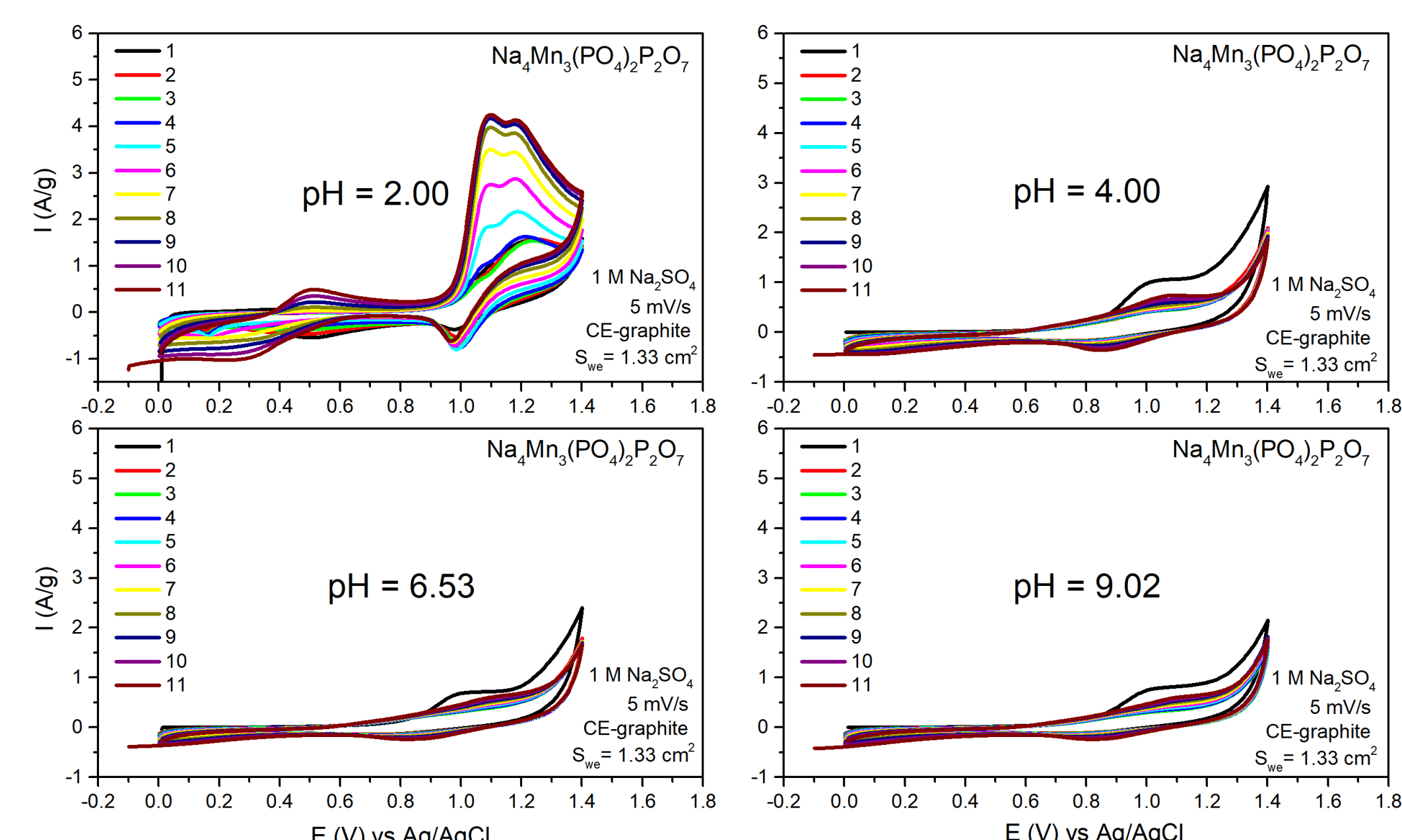


Fig. 5. Cyclic voltammograms of $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ at different pH

Conclusions

- Pure phases of $\text{Na}_3\text{MnPO}_4\text{CO}_3$ and $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ were synthesized by hydrothermal and solid-state methods, accordingly.
- Sample of $\text{Na}_3\text{MnPO}_4\text{CO}_3$ has 13,7% of carbon, while $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, which was coated with glucose, has only 5.9%.
- Ionic conductivity of both samples were measured and have sufficient values.
- Potentiostatic measurements of cyclic voltammograms of both samples were performed at different pH. Results show that samples are the most stable when pH is about 7.
- Both Mn-based mixed-phosphate materials are not stable enough for aqueous Na-ion batteries and must be modified.