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EXTENDED ABSTRACT

**Comparison of lithium and sodium intercalation materials\***

MILICA VUJKOVIĆ\*

*Faculty of Physical Chemistry, University in Belgrade, Studentski trg 12,  
11000 Belgrade, Serbia*

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**Abstract:** The low abundance of lithium in the Earth's crust and its high participation in overall cost of lithium-ion batteries incited intensive investigation of sodium-ion batteries, in the hope that they may become similar in their basic characteristics: specific energy and specific power. Furthermore, over the last years, research has been focused on the replacement of the organic electrolytes of Li- and Na-ion batteries by aqueous electrolytes, in order to simplify the production and improve safety of use. In this lecture, some recent results on selected intercalation materials are presented: layered structure vanadium oxides, olivine and nasicon phosphates, potentially usable in both Li and Na aqueous rechargeable batteries. After their characterization by X-ray diffraction and electron microscopy, the electrochemical behavior was studied by both cyclic voltammetry and chronopotentiometry. By comparing the intercalation kinetics and coulombic capacity of these materials in LiNO<sub>3</sub> and NaNO<sub>3</sub> solutions, it was shown that the following ones: Na<sub>1,2</sub>V<sub>3</sub>O<sub>8</sub>, Na<sub>2</sub>V<sub>6</sub>O<sub>16</sub>/C, NaFePO<sub>4</sub>/C and NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C may be used as electrode materials in aqueous alkali-ion batteries.

**Keywords:** sodium and lithium storage capacity; metal-ion aqueous batteries.

Thanks to their excellent electrochemical performance, such as high voltage (3–5 V) and high specific energy density (150–200 Wh kg<sup>-1</sup>), Li-ion batteries with organic electrolytes are widely used as power sources in portable electronic devices (mobile phones, laptops, digital cameras, *etc.*) and are regarded as one of the best alternative to fossil fuels in electric vehicles. They were commercialized in the early 90-ties. The first Li-ion battery was produced by the Sony Company in 1991 and consisted of a graphitic carbon anode, a LiCoO<sub>2</sub> cathode, and LiPF<sub>6</sub> dissolved in an organic solvent (mixture of ethylene carbonate and dimethyl car-

\* E-mail: milicavuj5@yahoo.com

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bonate) as electrolyte. This battery type is used in the majority of modern portable electronic devices.<sup>1</sup> Recently, Na-ion batteries have attracted increasing attention of researchers, expressed through the rising number of publications on sodium intercalation materials and sodium ion batteries, but a commercial model has not yet appeared on the market. Na-ion batteries are identical in their working principle to Li-ion batteries. Namely, in both, conductive electrolyte shuttles ions ( $\text{Li}^+$  or  $\text{Na}^+$ ) between the positive and negative electrode materials during charging and discharging. The main reasons for using sodium instead of lithium are higher abundance, lower price and comparable energy density. Although the ionic radius of  $\text{Na}^+$  is somewhat higher than that of  $\text{Li}^+$ , this is not always a substantial obstacle for efficient intercalation ability. It was evidenced in the literature that many lithium intercalation materials (V-, Mn- and Ti-based oxides, olivine  $\text{LiFePO}_4$ , nasicon structures, sulfate compounds, etc.) are also able to intercalate sodium. Contemporary research is also directed to the development of Li-ion and Na-ion batteries with aqueous electrolytes. The reasons are higher environmental friendliness and easier production of batteries with aqueous electrolytes.<sup>2</sup>

The presented lecture delivers an overview of the electrochemical behavior of several materials types synthesized in various ways (layered Na-vanadium oxides, olivine and nasicon phosphate), in Li- and Na-containing, aqueous electrolytic solutions.<sup>3-5</sup> The intercalation kinetics and intercalation capacity of these materials were evaluated and compared with respect to their applicability in lithium-ion or sodium-ion aqueous rechargeable batteries. It was shown that structure, morphology and chemical composition determine the electrochemical performance of materials in aqueous electrolytic solution, and lead to some difference in the coulombic capacities.

Unlike  $\text{Li}_{1.2}\text{V}_3\text{O}_8$ , which is one of the most investigated materials for Li-ion aqueous rechargeable batteries, the electrochemical behavior of  $\text{Na}_{1.2}\text{V}_3\text{O}_8$  in aqueous electrolyte was practically unknown.  $\text{Na}_{1.2}\text{V}_3\text{O}_8$  has a larger interlayer distance and higher chemical diffusion coefficient than  $\text{Li}_{1.2}\text{V}_3\text{O}_8$ . Recently, a paper regarding the electrochemical behavior of one-dimensional  $\text{Na}_{1.2}\text{V}_3\text{O}_8$  micro/nano belts synthesized by sol-gel method, in aqueous solutions of  $\text{LiNO}_3$ ,  $\text{NaNO}_3$  and  $\text{Mg}(\text{NO}_3)_2$  was published.<sup>4</sup> The capability to intercalate ions of different radii makes this material promising for Li, Na and Mg aqueous rechargeable batteries. Apart from  $\text{Na}_{1.2}\text{V}_3\text{O}_8$ , a hydrothermally synthesized  $\text{Na}_2\text{V}_6\text{O}_{16}/\text{C}$  composite was also found to be an excellent bifunctional material for Na and Li aqueous rechargeable batteries. The micro/nano belt-like morphology of  $\text{Na}_2\text{V}_6\text{O}_{16}/\text{C}$  was also obtained but spherical particles ( $\approx 50$  nm), caused by the presence of the carbon nanoparticles, were also observed. The presence of a few anodic and cathodic redox peaks in the CVs of both layered oxides  $\text{Na}_{1.2}\text{V}_3\text{O}_8$  and  $\text{Na}_2\text{V}_6\text{O}_{16}/\text{C}$  measured in  $\text{LiNO}_3$  and  $\text{NaNO}_3$ , indicated successful intercal-

ation of  $\text{Na}^+$  and  $\text{Li}^+$  into energetically non-equivalent tetrahedral positions. Higher Li *vs.* Na capacity was measured for both layered oxides. There is some theoretical prediction that an open-layered structure can easier accommodate larger  $\text{Na}^+$ , but this was not the case with these belt-like morphologies. Here, the ionic radius is the key factor that determines the diffusion rate through the layered structure and thus, the intercalation ability.

Contrary to the vanadate-layered structure, it was found that olivine and nasicon structures may be synthesized in a way to exhibit higher Na *vs.* Li storage capacity in an aqueous electrolyte, in spite of the unfavorable differences in ionic radii. Such behavior makes these materials very promising for use in aqueous Na-ion batteries. Olivine  $\text{LiFePO}_4/\text{C}$  and nasicon  $\text{NaTi}_2(\text{PO}_4)_3/\text{C}$ , synthesized by a gel-combustion procedure, exhibited the same morphology, consisting of agglomerated spherical particles with an average particle size of 75 nm.  $\text{LiFePO}_4$  incorporated in a carbon matrix<sup>3</sup> showed very fast kinetics of lithiation/delithiation in aqueous  $\text{LiNO}_3$  solution. This composite was successfully transformed into  $\text{NaFePO}_4/\text{C}$  by electrochemical replacement Li by Na ions in a saturated aqueous solution of  $\text{NaNO}_3$ . The delithiated  $\text{FePO}_4/\text{C}$  composite demonstrated the very high storage capacity of  $118 \text{ mAh g}^{-1}$  at  $10 \text{ mV s}^{-1}$  in  $\text{NaNO}_3$ , *i.e.*, two times higher than the corresponding storage capacity in  $\text{LiNO}_3$ .<sup>3,5</sup> One of the reasons for this is the weaker  $\text{Na}^+-\text{PO}_4^{3-}$  bond when compared to the  $\text{Li}^+-\text{PO}_4^{3-}$  bond. Cyclic voltammetry, in the combination with X-ray analysis, showed that the sodiation/desodiation reaction of  $\text{NaFePO}_4/\text{C}$  in  $\text{NaNO}_3$  goes through the formation of the intermediate phase  $\text{Na}_{0.7}\text{FePO}_4$ <sup>6</sup> and its efficiency strongly depends on the applied current.

An aqueous type of sodium rechargeable battery consisting of  $\text{Na}_{1.2}\text{V}_3\text{O}_8$  as the anode material<sup>4</sup> and olivine  $\text{LiFePO}_4/\text{C}$ <sup>3</sup> as the cathode material was fabricated and tested. The battery delivered very high currents with a quite good cyclic stability (80 % of the initial capacity) after 1000 charging/discharging cycles. The main problem of this battery for commercial purpose was its low average voltage, which is a general problem with aqueous batteries. In order to enhance the voltage, the employment of another anode material, such as nasicon  $\text{NaTi}_2(\text{PO}_4)_3$ , could be a good choice, thanks to the low redox potential of this material ( $-0.6 \text{ V vs. NHE}$ ). This compound is well known as a Na superionic conductor, and its theoretical capacity is  $133 \text{ mAh g}^{-1}$ . Both cyclic voltammetric and chronopotentiometric measurements of gel-combustion synthesized  $\text{NaTi}_2(\text{PO}_4)_3/\text{C}$  displayed faster diffusion of  $\text{Na}^+$  ions *vs.*  $\text{Li}^+$ , which is advantageous for the purposes of sodium aqueous rechargeable batteries.

ИЗВОД  
ПОРЕЂЕЊЕ МАТЕРИЈАЛА ЗА ИНТЕРКАЛАЦИЈУ ЛИТИЈУМА И НАТРИЈУМА

МИЛИЦА ВУЈКОВИЋ

Факултет за Физичку хемију, Универзитет у Београду, Студентски бр 12, 11000 Београд

Ниска заступљеност литијума у Земљиној кори и његово високо учешће у укупној цени литијум-јонских батерија подстиче истраживаче да интензивно истражују натријум-јонске батерије, у нади да оне могу бити сличне у основним карактеристикама: специфична енергија и специфична снага. Последњих година истраживачи се фокусирају на замену органских електролита литијум и натријум јонских батерија, са воденим електролитичким раствором, са циљем да поједноставе производњу и побољшају безбедност батерије. У овом предавању, приказани су резултати неколико интеркалатних материјала: слојевити оксиди ванадијума, оливин- и насикон-фосфати, који могу да се користе и у литијум и у натријум јонским секундарним батеријама. После њихове карактеризације рендгеноструктурном анализом и електронском микроскопијом, електрохемијско понашање испитано је цикличном волтаметријом и хронопотенциометријом. Поређећи кинетику интеркалације/деинтеркалације и кулонски капацитет ових материјала у  $\text{LiNO}_3$  и  $\text{NaNO}_3$ , показано је да следећи материјали  $\text{Na}_{1.2}\text{V}_3\text{O}_8$ ,  $\text{Na}_2\text{V}_6\text{O}_{16}/\text{C}$ ,  $\text{NaFePO}_4/\text{C}$  и  $\text{NaTi}_2(\text{PO}_4)_3/\text{C}$  могу да се користе као електродни материјали у воденим алкал-јонским батеријама.

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