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New Phosphate-based Electrode Material for High Performance Sodium-Ion Batteries

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Abstract*—A new Nasicon-type phosphate $Na_3ZrCo(PO_4)_3$ is successfully synthesized using a sol-gel method. In this study, we investigate the synthesis, structural and electrochemical properties of this 3D phosphate. The Rietveld refinement of the XRD pattern showed that at room temperature, the material exhibits a hexagonal symmetry with the space group (R-3) and the cell parameters a = 8.931(3) Å; c = 22.310(1) Å. The structure of $Na_3ZrCo(PO_4)_3$consists of edge sharing [MO6] octahedra (M = Zr, Co) resulting in chains parallel to [−101]. These chains are linked together via the [PO4] tetrahedra to form two distinct tunnels in which sodium cations are located. The synthesized $Na_3ZrCo(PO_4)_3$were tested in sodium half-cell.An initial discharge capacity of 120 mAhg^{-1} at C/20 for the first cycle and good capacity retention at high rates were obtained.

Keywords-Sodium-ion batteries (NIBs), NaSICON, Cathode, Phosphate, Energy Storage.

I. INTRODUCTION

The search for new electrode materials is a collective responsibility for the well-being of our community. In this context, the environment, the cost and the safety are the challenges that should be considered consecutively in the field of energy production and storage.

The very rapid development of embedded devices in electric vehicles (EVs), hybrids (HEVs) and satellites, portable electronics (smart phones, tablets and laptops), and also alternative energies, such as wind or solar, has led to very strong demand for lithium-ion batteries around the world (1). The cost of this item continues to increase. Its low availability and its geographical distribution, very uneven around the planet: China and South America (Bolivia, Chile and Argentina) are major drawbacks. The use of another alkaline element such as sodium has tobe considered for theupcoming years. Indeed, Sodium-ion batteries (SIBs) can be regarded as the optimal solution that meets the requirements of our current world (2), namely: sustainable development (3), safety and reasonable price (4).

Due to its high sodium ion conductivity (5-7), the Nasicon-type materials has been extensively studied (8-10).Recently, much attention has been focused to manganese-based polyanionic compounds (11-14). But this kind of manganese-based polyanionic compounds present a lot of Weaknesses such as Jahn-Teller distortions caused byMn^{3+} and its disproportionation reaction leading to the dissolution of Mn^{2+} in the existingliquid electrolyte.

In order to avoid all these weaknesses and explore the electrochemical performance of polyanionic compounds, manganese was substituted by cobalt to obtain a new compound cobalt-based polyanionic.

In this paper, we report the preparation of bare and carbon-coated $Na_3ZrCo(PO_4)_3$. The samples were characterized by X-ray diffraction analysis, examined via Scanning Electron Microscopy and electrochemically tested in Na half cells.

II. EXPERIMENTAL

A. Material preparation

$Na_3CoZr(PO_4)_3$material was obtained through a Sol-Gel reaction process from aqueous solutions of $CoCl_2.6H_2O$, $ZrOCl_2.8H_2O$ and $(NH_4)_2HPO_4$ and acidic solution of Na_2CO_3. The mixture was stirred for 30 minutes and heated up to 60°C until complete evaporation of the solution and gel formation. The resulting residue was heated at temperatures between 200-750 °C. Intermediate grindings were performed on the sample before each calcination step.

B. Carbon-coating process

For carbon-coating procedure,85 wt.% of the obtained powder was intimately mixed andgrinded with sucrose (15 wt. %) using pure acetone solution (99%) followed by firing at 600 °C for 5h in Ar flow. The obtained cathode material was referenced to asNaZrCoP/C.

C. Structure and Morphological Characterization

The XRD analyzes were carried out using a "BRUKER D8 ADVANCE" diffractometer with a Cu Kα radiation source (λ = 1.54056 Å). The structure of the $Na_3CoZr(PO_4)_3$ phosphate compound was derived from the step-scanned X-ray intensity data, in the range 10–120° (2θ) with a step size of 0.01° (2θ) and counting time of 10s for each step. The structural parameters were refined by the Rietveld method, using the computer program FULLPROF (7). The morphology of NaZrCoP/C have been identified using Emission Scanning Electron Microscopy (SEM, FEG 450). The SEM images were obtained at a vacuum level of below 10−5 mbar with an accelerating voltage of 5 kV.

D. Electrode preparation & battery assembly

The slurry preparation consists of mixing NaZrCoP/C composite with CarboxyMethyl Cellulose (CMC) as binder and carbon black as a conductive agent in a weight ratio of 80:15:05.

The suspension was left under magnetic stirring (450 rpm speed) overnight, then poured on aaluminum foil using doctor Blade technique. Finally, the slurry was dried at 80 °C for 4 h in a convection oven, punched into disks with 10 mm diameter, then dried overnight at 120 °C under vacuum to remove any traces of solvent or moisture. The loading of active materials of about 1.5 mg cm-2 .

Carbon-coated NaSICON-type NaZrCoP was tested versus metallic sodium in half-cells. Coin cells (CR2032) assembly was carried out in an argon-filled glove box (Jacomex, France), using Whatman sheets soaked with 1.0 M $NaClO_4$dissolved in Propylene carbonate (PC).

III. RESULTS AND DISCUSSION

A. Crystal structure

Figure 1 shows the powder diffraction pattern of $Na_3CoZr(PO_4)_3$. All the peaks in the pattern can be indexed to the hexagonal NaSICON structure with the space group R-3c (N°167). The unit cell parameters and the unit cell volume calculated from the pattern profile matching of the $Na_3CoZr(PO_4)_3$ pattern are respectively: a = 8.931(3)Å ; c = 22.310(1) Å.

The atomic coordinates of $Na_3MgZr(PO_4)_3$homologous phosphate was used as a starting model for the structural refinement of the studied sample. The structure of $Na_3CoZr(PO_4)_3$consists of a three-dimensional framework constructed by the phosphate octahedral PO4 and the Cobalt/Zirconium octahedral Co/ZrO6 sharing their corners (see inset of Figure 1). The sodium cations are in both NaSICONsites M(1) and M(2).

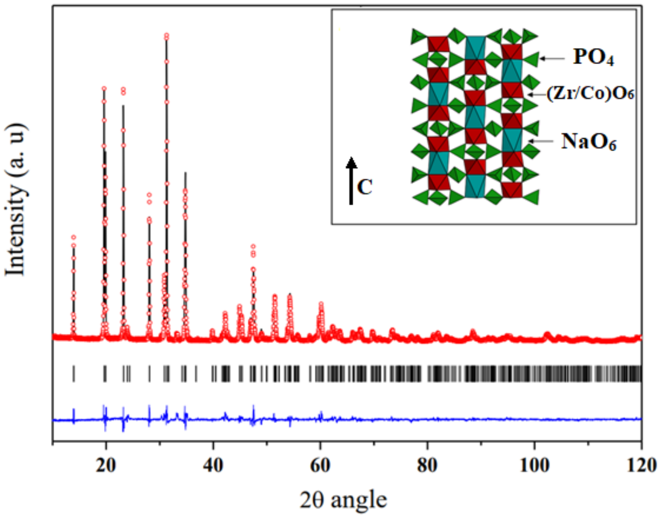

Figure 1: Observed and calculated XRD pattern of $Na_3CoZr(PO_4)_3$: experimental data (red spheres), calculated pattern (black line), Bragg positions (green bars) and difference curves (blue line). Inset figure presents the crystal structure of $Na_3CoZr(PO_4)_3$.

B. Morphological Characterization

The morphology of the $Na_3CoZr(PO_4)_3$/C composite was examined via Scanning Electron Microscopy. Figure 2 shows

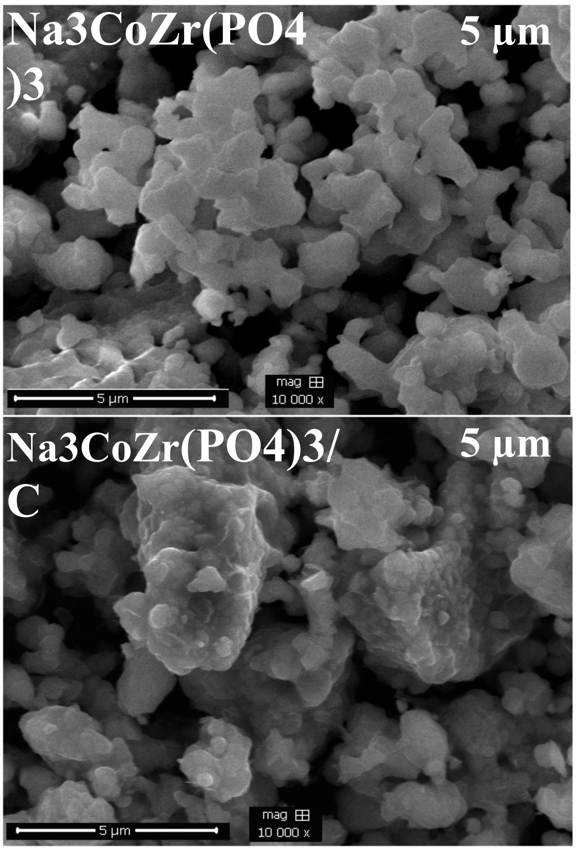

Figure 2: SEM pictures of (a) uncoated and(b) coated$Na_3ZrCo(PO_4)_3$.

the SEM imagesof our materiel beforeand after carbon coating.The particles have an irregular shape and exhibit a micrometric size. We note the presence of agglomerates as it can be seen from Figure 2b.

C. Electrochemical properties

Cyclic Voltammetry was performed for $Na_3CoZr(PO_4)_3/C$ at the scanning rate 0.01mV s^{-1} in the potential range of 3.5-4.3V versus Na/Na^+. As presented in Figure 3, the strong similarity between the charge/discharge curves indicates the reversibility of the electrochemical sodiation/desodiationNaZrCoP/C. Anodic and cathodic peakswereobserved at the voltage 4.15 and 4.05 versus Na/Na^+ which can be assigned to the oxidation/reduction of cobalt (Co^{2+}/Co^{3+}). In addition, no large difference in the position of anodic and cathodic peaks was noticed suggesting similar kinetics upon charge/discharge.

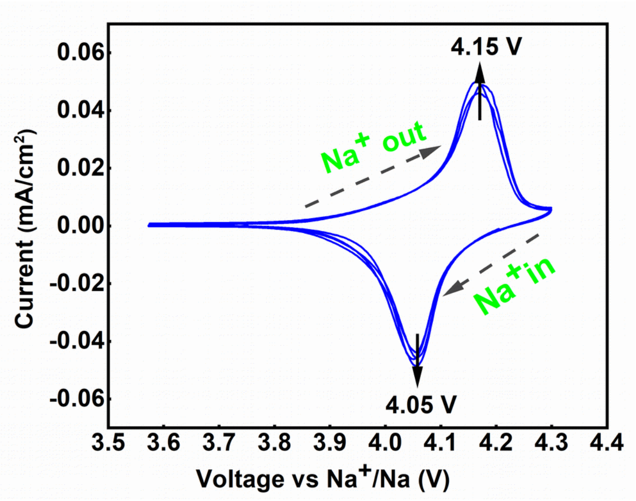

Figure 3. Cyclic voltammetry profiles of the $Na_3CoZr(PO_4)_3/C$ at a scan rate of 0.01 mV s^{-1}.

Following the cyclic voltammetry studies, charge-discharge measurements were carried out for $Na_3CoZr(PO_4)_3/C$ at C/20 in the voltage range from 2 to 4.3V versus Na^+/Na. $Na_3CoZr(PO_4)_3/C$ exhibits an initial charge capacity of 120mAhg^{-1}. One reversible plateau was observed during the charge and discharge at 4.15 and 4.05V, respectively, which is in good agreement with the CV results. From the 1st to the 15th cycle, the charge/discharge curves exhibit the same characteristics and features indicating a reversibility in the process.

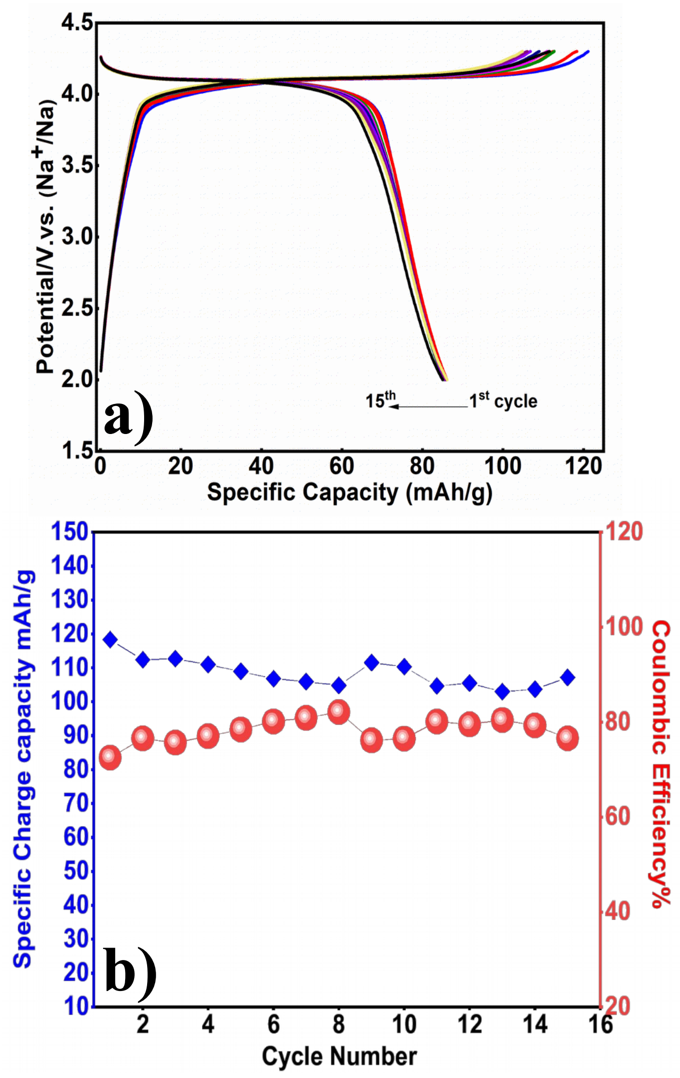

Figure 4: a) Discharge/ charge curves of $Na_3CoZr(PO_4)_3/C$ tested at C/20 within the voltage range 2.0 V – 4.3 V; b)Discharge capacity and coulombic efficiency vs. cycle number of $Na_3CoZr(PO_4)_3/C$ testing at C/20 current rate within 2.0 V– 4.3 V voltage range.

CONCLUSION & PERSPECTIVES

New NaSICON-type phosphate $Na_3CoZr(PO_4)_3$ was successfully prepared using the sol-gel method and coated using sucrose as the carbon source. The Rietveld refinement of the XRD pattern showed that at room temperature, the material has a hexagonal symmetry with the space group (R-3c). This compound presents an initial charge capacity of 120mAhg^{-1} at C/20 in the voltage range of 2.0 -4.3V. The charge/discharge profile curves have shown a reversibility in the electrochemical process. Two peaks assigned to the redox couple $Co^{2+}/^{Co3+}$ were observed respectively at 4.15 and 4.05V versus Na^+/Na. Optimization of coating/cell design and investigation of magnetic/optical properties are in progress.$Na_3CoZr(PO_4)_3/C$ can be regarded as potential candidate for next generation sodium ion batteries.

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