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Solution-assisted Energy-savvy Synthesis of High-voltage $Na_2M_2(SO_4)_3$ (M = 3d metals) Alluaudite Family of Sodium Insertion Materials

D. Dwibedi[a], P. Barpanda[a,]*

[a] *Faraday Materials Laboratory, Materials Research Center, Indian Institute of Science, Bangalore, India*

Abstract

The benchmarking of Fe^{3+}/Fe^{2+} redox potential at 3.8 V (versus Na) in alluaudite-type $Na_2Fe_2(SO_4)_3$, along with fast rate kinetics and excellent cycling stability (Nat. Commun., 5, 4358, 2014) has opened up new era of research in Na-ion research. Further insight to the reported material show synthesis is a careful solid-state method involving (a) formation of anhydrous $FeSO_4$ from commercial $FeSO_4.7H_2O$, (b) prolonged milling and (c) longer annealing (350°C, 24 h). Journey of such materials from laboratory to industry warrants economic, sustainable and scalable synthesis. Here, we report novel solution assisted-Ionothermal, aqueous spray-drying and pechini synthesis of $Na_2Fe_2(SO_4)_3$, [M = 3d metals] alluaudite cathodes. It will approach (i) salient feature of synthesis, (ii) structure/ polymorphism, (iii) magnetic properties and (iv) electrochemical properties of $Na_2Fe_2 (SO_4)_3$ cathode materials.

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Keywords: Sodium batteries; cathode; alluaudites; aqueous synthesis

1. Introduction

Scarcity of lithium containing minerals has notably decreased the endorsement of lithium ion batteries in large scale energy storage application. This parallely rose a thrust of research in potential price alternative sodium ion

* Corresponding author. Tel.: (+91) 80 22932783, Fax: (+91) 80 23607316.
E-mail address: smita@mrc.iisc.ernet.in

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batteries, owing to its abundancy, nontoxicity and good geographical distribution. In this account, plethora of Fe based cathode materials which favours sodium intercalation has been explored.[1-2]. One such Na based alluaudite type sulphate frame work $Na_2Fe_2(SO_4)_3$, developed from low cost precursors, recently has benchmarked Fe^{3+}/Fe^{2+} redox potential at 3.8 V vs. Na with excellent cyclability and rate kinetics [1]. This material can be synthesized carefully by solid state method involving 3 steps; a) Making of anhydrous $FeSO_4$ from commercial $FeSO_4.7H_2O$, b) prolonged mixing and c) extended annealing (350°C, 24 h) which as a whole is tedious. Commercialization demands performance and low cost. Motivation of this work was to optimize synthesis in a way to attain; a) reduced cost, b) energy saavy, c) scalable product. In this pursuit, we explored some unconventional solution assisted synthesis- Ionothermal, Spray drying, Pechini method. Solution assisted synthesis has advantage over reported solid state synthesis in means of reducing time or temperature or both, since diffusion of ions in liquid is faster than solid. The current work extends to other members of the family to explore the structure and polymorphism if any. Finally electrochemistry of different synthesized material is investigated.

2. Salient features of synthesis

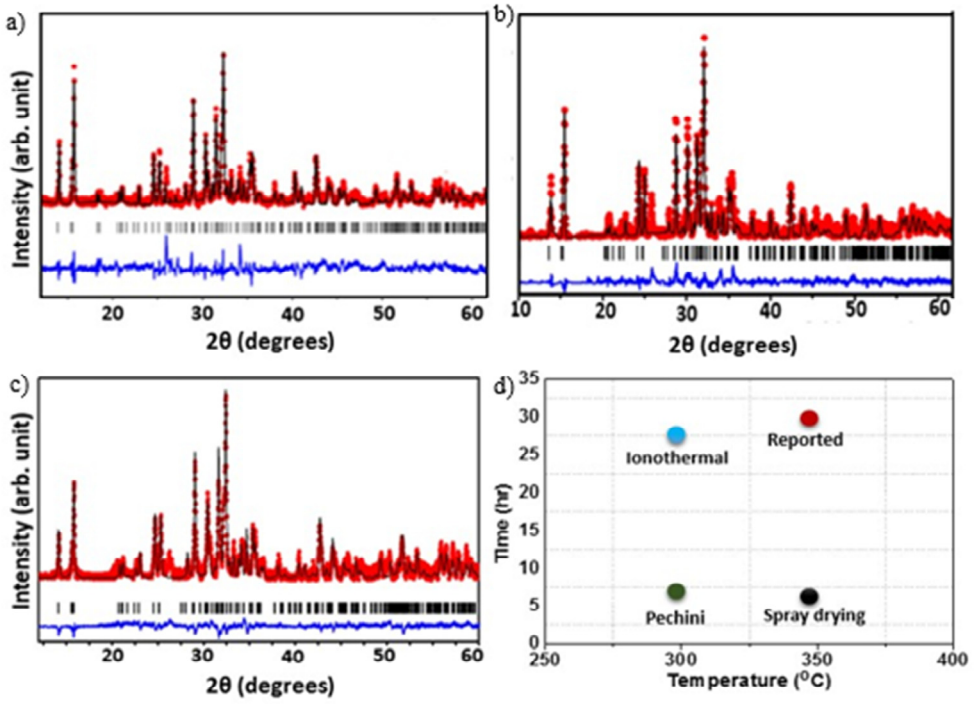

Fig. 1. (Rietveld refined XRD patterns of; a). Ionothermal; b). Spray drying; c). Pechini synthesized $Na_2Fe_2(SO_4)_3$ d). Time vs Temperature plot of discussed synthesis.

2.1. Ionothermal Method

Ionothermal synthesis parallels hydrothermal synthesis; except that solvent is ionic liquid. Ionic liquid in a broad way is any material which in liquid state is predominantly of ionic species [3]. This fecilates an additional properties of being used as structure directing agent. For synthesis of $Na_2Fe_2(SO_4)_3$, we used Na_2SO_4 and $FeSO_4.H_2O$ as precurssors and EMI-TFSI ionic liquid as solvent. Precurssors were partially dissolved in ionic liquid in teflon container of bomb. The reaction proceeded at 300°C for 30h in ambient atmosphere. The resulting product was centrifuged and used for structural analysis. XRD pattern and pattern fitting in Fig. 1(a). confirmed product formation. With this synthesis we could achieve the lowest ever synthesis temperature at 300 °C.

2.2. Spray Dry Method

In Spray dryer we introduce a fine spray of the liquid product into a hot stream of air that evaporates the water leaving a powder to fall and be collected. The feed material and hot air enters the chamber in same inlet in same direction. High turbulence of hot air instantly atomizes the liquid and well mixed intermediate product falls under gravity and collected. This method ensures atomic level mixing keeping the ionic state of product intact. We employed the unconventionality of the method in our synthesis and introduced first aqueous based synthesis with sulphate precurssors Na_2SO_4 and $FeSO_4.7H_2O$. The intermediate product from spray drying is annealed at 350°C for 8h in argon ambience. XRD and pattern fitting of resulting product in Fig 1(b) matches with standard one.

2.3. Pechini Method

Pechini is another 2 step aqueous based synthesis. The speciality of this method lies in using a complexing agent. During the reaction complexing agent holds metal ions by ligand formation and up on annealing it leaves leading to final product formation. In this the oxidation state of the ions is ensured. Because of aqueous media, the synthesis gives clue of faster kinetics. Following the method we took our precursor Na_2SO_4, $FeSO_4.7H_2O$ & complexing agent as $Na_2O_8C_{10}H_{14}N_2.2H_2O$ (triplex-III) and dissolved in aqueous media which was heated at 100°C to evaporate water. The intermediate gel type product was then annealed at 350 °C for 6h in argon ambience. Structural characterization in Fig 1(c) confirms product formation. With this synthesis we report lowest ever synthesis time.
All the method discussed above is scalable for industrial demands. We summarize all above synthesis with the reported synthesis in a time vs temperature plot In Fig. 1(d).

3. Unfolding other members of alluaudites

$Na_2M_2(SO_4)_3$ [M = 3d metals] constitutes alluaudite family of materials. It is always exiting to explore the structure of other family members when one of them exhibits extraordinary properties. Hence forth following above synthesis and stoichiometry $Na_2Mn_2(SO_4)_3$, $Na_2Co_2(SO_4)_3$, $Na_2Ni_2(SO_4)_3$ was made. Structural characterization reveal $Na_2Mn_2(SO_4)_3$ to adopt C2/c geometry which is same as the reported iron analogue. Owing to its comparatively smaller size Ni based $Na_2Ni_2(SO_4)_3$ adopts $P2_1/c$ geometry. The interesting result was with $Na_2Co_2(SO_4)_3$. Two different synthesis gave two different structure. Pechini synthesis yielded result $P2_1/c$ geometry which is as Ni analogue.

Solid state synthesis resulted C2/c geometry which is as Mn analogue. XRD pattern in Fig. 2 shows polymorphism in $Na_2Co_2(SO_4)_3$.

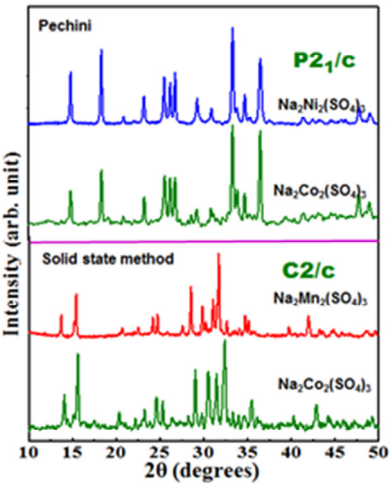

Fig. 2. XRD pattern of $Na_2Mn_2(SO_4)_3$, $Na_2Co_2(SO_4)_3$ & $Na_2Ni_2(SO_4)_3$.

4. Electrochemical properties of $Na_2Fe_2(SO_4)_3$

Electrochemical studies were carried out with the active material in a half cell. Measurements were done at C/20 rate in room temperature. Measurements reveal electrochemical activity between 3.4-4.2V (Fig. 3 (a)). Voltage drop from first to second charge is noticed, which can be associated with irreversible structural change during cycling. Excellent cycling stability is observed with average redox potential located at 3.6-3.8 V (Fig. 3 (b)). Reversible capacity of 80mAh/g is achieved which is 80 percent of theoretical capacity.

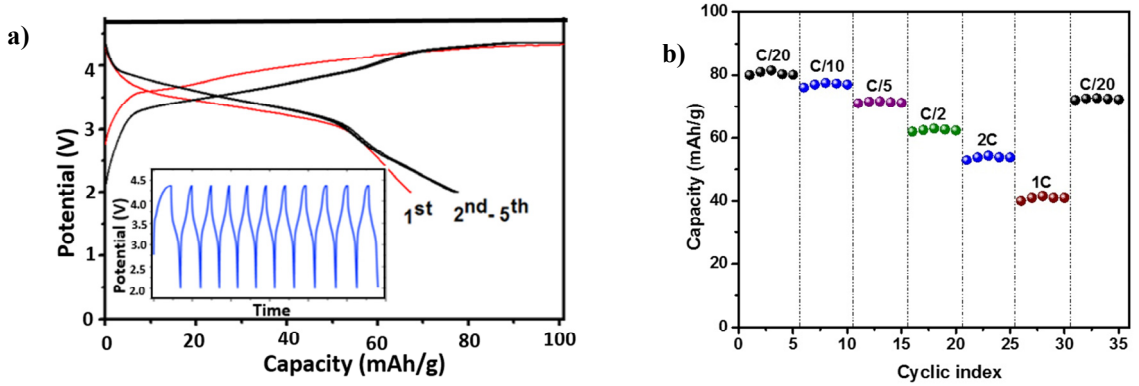

Fig. 3. Electrochemistry of $Na_2Fe_2(SO_4)_3$ (a) galvanostatic charge discharge profile and (b) capacity at different rates.

5. Conclusions

Sulphate based $Na_2Fe_2(SO_4)_3$ alluaudite has been explored as high voltage 3.8 V material. Substituting the tedious solid state method for the material synthesis, we have reported some simple and sustainable way of synthesis as 1. Ionothermal, 2. Spraydrying 3. Pechini methods. Current study discusses various salient features of ionothermal, spray drying, Pechini synthesis, which gives comparable electrochemical properties of reported $Na_2Fe_2(SO_4)_3$ alluaudite.

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