

The 2017 H. H. Uhlig Summer Research Fellowship – Summary Report: Design of New Electrode Materials for Na-Ion Batteries from the Alluaudite Minerals

To cite this article: Debasmita Dwibedi 2017 *Electrochem. Soc. Interface* **26** 96

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THE 2017 H. H. UHLIG SUMMER RESEARCH FELLOWSHIP – SUMMARY REPORT

Design of New Electrode Materials for Na-Ion Batteries from the Alluaudite Minerals

by Debasmita Dwivedi

To empower an increasingly diverse range of energy-intensive applications, electrochemical energy storage in general and Li-ion batteries (LIB) in particular have become key players. But now they are at a critical juncture due to limited lithium resources, which has rekindled a growing interest in Na-ion batteries (NIB) for mass storage applications. This viability of NIB has led to an intensive exploration of wide range of “cathode materials.” In this regard, several strategies can be pursued like high-throughput materials computation to design new materials with “magic phase composition” having both high voltage and high capacity, but success here is still limited. Another interesting way, which we pursued, is to browse through well-known minerals to spot families of materials having attractive structural features for ion transport. One such family is alluaudites with the general formula: $\text{Na}_2\text{M}_2(\text{XO}_4)_3$ ($\text{M} = 3d$ metals; $\text{X} = \text{S}, \text{P}$ etc.).¹⁻⁵ A recent report by Barpanda, et al., unveiled the extraordinary electrochemical activity of $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ alluaudites benchmarking the highest ever $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential (ca. 3.8 V vs. Na^+/Na^0).² With this as the basis, we framed our investigation to explore/design new electrode materials from this alluaudite family.

The motivation was: (i) to design new alluaudite electrodes with low cost and easily scalable synthesis; (ii) to investigate their structural features and ion migration pathways; and (iii) to tune their electrochemical activity, thereby establishing the synthesis-structure-property correlation of alluaudites. In this pursuit, at first, we explored some unconventional solvothermal routes: (i) ionothermal,⁴ (ii) spray drying; and (iii) Pechini synthesis. Their unique attributes with reported synthesis are highlighted in Table I. Indeed, these solvothermal routes fulfil the demand of designing efficient electrodes economically.

As we know from the inductive effect principle, in polyanionic cathodes ($\text{M}-\text{XO}_n^m$), the ionic bonding nature of M can be tuned depending on the nature of XO bonding. If X is more electronegative, it forms a stronger bond with O, thereby making the M-O bond more ionic. Further in the ionic M-O bond, the lower repulsion between bonding and anti-bonding orbitals places the orbital far from the Fermi level, thereby yielding a higher redox voltage. Employing this, we extended our search for high-voltage cathodes to isostructural analogues and discovered two novel alluaudites: 4.4 V $\text{Na}_{2.44}\text{Mn}_{1.78}(\text{SO}_4)_3$ and 5 V $\text{Na}_{2.37}\text{Co}_{1.83}(\text{SO}_4)_3$.^{4,5} Further, with

different Pauling electronegativity values, changing X should follow a general voltage trend of $\text{Mo} < \text{V} < \text{P} < \text{S}$. In this series, we started with the high-throughput synthesis and structural analysis of the phosphate alluaudite framework. For the first time, we successfully synthesized phosphate alluaudite $\text{NaFe}_2\text{Mn}(\text{PO}_4)_3$ by solution combustion synthesis at 600 °C that exhibited 3.0 V redox potential and 75% of the theoretical capacity with good cycling stability. The redox potential tunability with sulphate and phosphate alluaudite is in accordance with inductive effect principle, as shown in Fig. 1.

This work, starting with various energy-savvy synthesis routes to discovery of new sulphate alluaudites and tuning the redox activity of phosphate alluaudites, attests the richness of alluaudites as potential sodium insertion hosts.

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DOI: 10.1149/2.F13174jf.

Acknowledgments

The author is grateful to The Electrochemical Society for the Herbert H. Uhlig Summer Fellowship and to Dr. Prabeer Barpanda for his constant motivation and guidance.

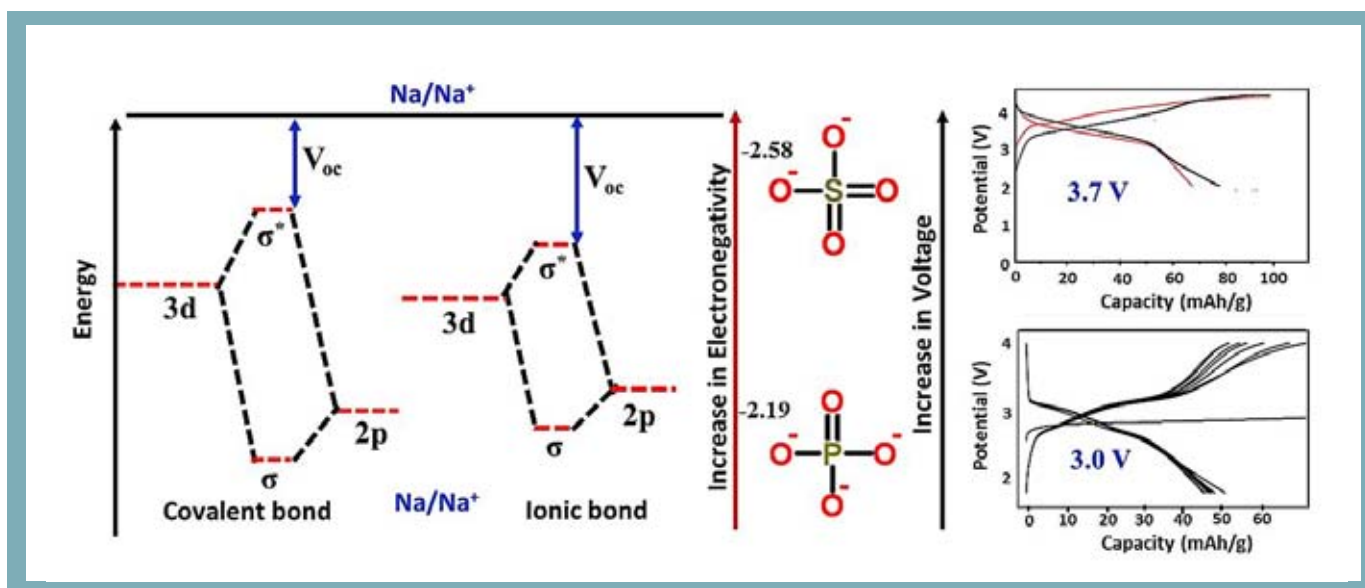
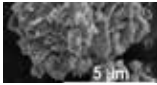
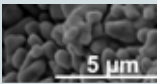
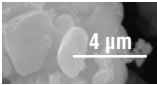



FIG. 1. Inductive effect demonstrating the tunability of redox potential in sulphate and phosphate alluaudites.


Table I. Highlights of various synthesis of $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ alluaudites.				
Employed Synthesis	Morphology	Time	Temperature	Electrochemistry*
Reported Solid-state Synthesis ²	 Agglomerated	12 h mill + 24 h annealing	350 °C	100 mAh/g Capacity** 3.8 V Potential
Ionothermal Route ³	 Bean shaped	30 h Annealing in air ambience	300 °C	80 mAh/g Capacity 3.7 V Potential
Spray drying Route	 Spherical	6 h Annealing	350 °C	75 mAh/g Capacity 3.7 V Potential
Pechini Synthesis	 Porous	6 h Annealing	200 °C	70 mAh/g Capacity 3.7 V Potential

*Cycling at C/20.
**Theoretical capacity.

About the Author



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