A Novel Ternary Ordered Intermetallics Cu₃ZnSb As Anode for Sodium-Ion StorageDebanjana Pahari^a, Samiran Misra^b, Partha P. Jana^b, Sreeraj Puravankara^{a*}^aSchool of Energy Science and Engineering, Indian Institute of Technology Kharagpur, Kharagpur - 721302, India^bDepartment of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur - 721302, India

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Introduction

- Tetragonal space group $P4/nmm$ (129)
- Lattice parameters $a = 4.2171$ (3) Å and $c = 8.6925$ (11) Å
- Alternating units of Cu₂Sb and CsCl type β'-brass (CuZn) structures in the [001]
- Theoretical charge capacity 212.83 mAhg⁻¹

Materials and Methods

Pure Cu + Zn + Sb

(i) 600 °C firing for 24 hr
Temperature ramp 2.4 °C/min

(iii) Cooled to 450 °C
Temperature ramp 0.2 °C/min

(ii) 900 °C firing for 12 hr
Temperature ramp 0.5 °C/min

(iv) Annealed for 96 hr
Cooled to room temperature

Cu₃ZnSb

Electrochemistry

- AM:Carbon:Binder = 80:10:10
- Electrode casted on Cu-foil
- Weight of AM = 1.8 mg/cm²
- Voltage range 0.005 – 2 V
- CR 2032 cells in two-electrode set-up
- Separator Whatman GF/C
- Reference electrode Li/Na metal
- Electrolyte 1 M NaClO₄ in EC + DEC (1:1 v/v) with and without additives (VC and FEC)

Result and Discussion

- Initial discharge capacity 300 mAhg⁻¹
- 4.2 Li-ion insertion
- Charge capacity 200 mAhg⁻¹
- 2.8 Li-ion removal

- Initial discharge capacity 323 mAhg⁻¹
- 4.5 Na-ion insertion
- Charge capacity 150 mAhg⁻¹
- 2.5 Na-ion removal

Ex-situ X-Ray measurements

- In the first discharged state,
- Lithiated Cu₂Sb peaks at 23° and 27° when discharged to 5 mV.
 - Sodiated CuZn peak at 22°
 - No sodiated Cu₂Sb peaks

Cycle-stability of Li intercalation

Electrode	1 st Charge Capacity (mAhg ⁻¹)	20 th Charge Capacity (mAhg ⁻¹)	Capacity retention (%)
0%	203.3	36	17.5
2% FEC	109.4	21.9	20
5% FEC	364.4	78.5	21.5
1% VC	180.3	66.5	36.9
3% VC	181.8	61.6	33.9

Conclusions

- A novel class of ternary ordered intermetallics has been successfully synthesized.
- Cu₃ZnSb electrodes are electrochemically active with both Li and Na in a distinctive fashion.
- Cu₂Sb layers are redox active with Li, where as Cu₂Sb as well as CuZn layers are redox active for Na.
- Inherent cyclic instability of the electrodes are improved through inclusion of additives into the electrolyte.

Acknowledgements

The authors are grateful for the support of this work to Indian Institute of Technology Kharagpur.

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