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comparison with reported CTS materials, CV curves, GITT calculations, CV calculations, and synthetic mechanisms (PDF)

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#### **Notes**

The authors declare no competing financial interest.

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# **REFERENCES**

- (1) Grey, C. P.; Tarascon, J. M. Sustainability and *In Situ* Monitoring in Battery Development. *Nat. Mater.* **2017**, *16*, 45–56.
- (2) Kwade, A.; Haselrieder, W.; Leithoff, R.; Modlinger, A.; Dietrich, F.; Droeder, K. Current Status and Challenges for Automotive Battery Production Technologies. *Nat. Energy* **2018**, *3*, 290–300.
- (3) Winter, M.; Besenhard, J. O. Electrochemical Lithiation of Tin and Tin-Based Intermetallics and Composites. *Electrochim. Acta* **1999**, 45, 31–50.
- (4) Huang, B.; Pan, Z.; Su, X.; An, L. Tin-Based Materials as Versatile Anodes for Alkali (Earth)-Ion Batteries. *J. Power Sources* **2018**, 395, 41–59.
- (5) Wei, Z.; Wang, L.; Zhuo, M.; Ni, W.; Wang, H.; Ma, J. Layered Tin Sulfide and Selenide Anode Materials for Li- and Na-Ion Batteries. *J. Mater. Chem. A* **2018**, *6*, 12185–12214.
- (6) Chao, D.; Ouyang, B.; Liang, P.; Huong, T. T. T.; Jia, G.; Huang, H.; Xia, X.; Rawat, R. S.; Fan, H. J. C-Plasma of Hierarchical Graphene Survives SnS Bundles for Ultrastable and High Volumetric Na-Ion Storage. *Adv. Mater.* **2018**, *30*, 1804833.
- (7) Zhao, Y.; Wang, L. P.; Sougrati, M. T.; Feng, Z.; Leconte, Y.; Fisher, A.; Srinivasan, M.; Xu, Z. A Review on Design Strategies for Carbon Based Metal Oxides and Sulfides Nanocomposites for High Performance Li and Na Ion Battery Anodes. *Adv. Energy Mater.* **2017**, 7, 1601424.
- (8) Xu, J.; Ma, J.; Fan, Q.; Guo, S.; Dou, S. Recent Progress in the Design of Advanced Cathode Materials and Battery Models for High-Performance Lithium-X ( $X = O_2$ , S, Se, Te,  $I_2$ ,  $Br_2$ ) Batteries. *Adv. Mater.* **2017**, 29, 1606454.
- (9) Arico, A. S.; Bruce, P.; Scrosati, B.; Tarascon, J. M.; van Schalkwijk, W. Nanostructured Materials for Advanced Energy Conversion and Storage Devices. *Nat. Mater.* **2005**, *4*, 366–377.

- (10) Wu, F.; Yushin, G. Conversion Cathodes for Rechargeable Lithium and Lithium-Ion Batteries. *Energy Environ. Sci.* **2017**, *10*, 435–459
- (11) Cabana, J.; Monconduit, L.; Larcher, D.; Palacin, M. R. Beyond Intercalation-Based Li-Ion Batteries: The State of the Art and Challenges of Electrode Materials Reacting through Conversion Reactions. *Adv. Mater.* **2010**, 22, E170–E192.
- (12) Palacin, M. R. Recent Advances in Rechargeable Battery Materials: A Chemist's Perspective. *Chem. Soc. Rev.* **2009**, *38*, 2565–2575.
- (13) Youn, D. H.; Stauffer, S. K.; Xiao, P.; Park, H.; Nam, Y.; Dolocan, A.; Henkelman, G.; Heller, A.; Mullins, C. B. Simple Synthesis of Nanocrystalline Tin Sulfide/N-Doped Reduced Graphene Oxide Composites as Lithium Ion Battery Anodes. *ACS Nano* **2016**, *10*, 10778–10788.
- (14) Lin, J.; Lim, J. M.; Youn, D. H.; Kawashima, K.; Kim, J. H.; Liu, Y.; Guo, H.; Henkelman, G.; Heller, A.; Mullins, C. B. Self-Assembled Cu-Sn-S Nanotubes with High (De)Lithiation Performance. *ACS Nano* **2017**, *11*, 10347–10356.
- (15) Bombicz, P.; Mutikainen, I.; Krunks, M.; Leskelä, T.; Madarász, J.; Niinistö, L. Synthesis, Vibrational Spectra and X-Ray Structures of Copper(I) Thiourea Complexes. *Inorg. Chim. Acta* **2004**, 357, 513–525.
- (16) Jagminas, A.; Niaura, G.; Judzentiene, A.; Juskenas, R. Spectroscopic Evidence of a Novel Array Ac Fabrication within the Alumina Template Pores from Acidic Cu(II)-Thiourea Solution. *Appl. Surf. Sci.* **2004**, 239, 72–78.
- (17) Petit, C.; Bandosz, T. J. Mof-Graphite Oxide Composites: Combining the Uniqueness of Graphene Layers and Metal-Organic Frameworks. *Adv. Mater.* **2009**, 21, 4753–4757.
- (18) Jahan, M.; Liu, Z.; Loh, K. P. A Graphene Oxide and Copper-Centered Metal Organic Framework Composite as a Tri-Functional Catalyst for Her, Oer, and Orr. *Adv. Funct. Mater.* **2013**, 23, 5363–5372.
- (19) Yang, D.; Velamakanni, A.; Bozoklu, G.; Park, S.; Stoller, M.; Piner, R. D.; Stankovich, S.; Jung, I.; Field, D. A.; Ventrice, C. A.; Ruoff, R. S. Chemical Analysis of Graphene Oxide Films after Heat and Chemical Treatments by X-Ray Photoelectron and Micro-Raman Spectroscopy. *Carbon* **2009**, *47*, 145–152.
- (20) Ferrari, A. C.; Basko, D. M. Raman Spectroscopy as a Versatile Tool for Studying the Properties of Graphene. *Nat. Nanotechnol.* **2013**, *8*, 235–246.
- (21) Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S. Synthesis of Graphene-Based Nanosheets *via* Chemical Reduction of Exfoliated Graphite Oxide. *Carbon* **2007**, *45*, 1558–1565.
- (22) Martin, L.; Martinez, H.; Poinot, D.; Pecquenard, B.; Le Cras, F. Comprehensive X-Ray Photoelectron Spectroscopy Study of the Conversion Reaction Mechanism of CuO in Lithiated Thin Film Electrodes. J. Phys. Chem. C 2013, 117, 4421–4430.
- (23) Hu, X.; Jia, J.; Wang, G.; Chen, J.; Zhan, H.; Wen, Z. Reliable and General Route to Inverse Opal Structured Nanohybrids of Carbon-Confined Transition Metal Sulfides Quantum Dots for High-Performance Sodium Storage. *Adv. Energy Mater.* **2018**, *8*, 1801452.
- (24) Lin, J.; Guo, J.; Liu, C.; Guo, H. Ultrahigh-Performance Cu<sub>2</sub>ZnSnS<sub>4</sub> Thin Film and Its Application in Microscale Thin-Film Lithium-Ion Battery: Comparison with SnO<sub>2</sub>. ACS Appl. Mater. Interfaces **2016**, 8, 34372–34378.
- (25) Qu, B.; Ma, C.; Ji, G.; Xu, C.; Xu, J.; Meng, Y. S.; Wang, T.; Lee, J. Y. Layered SnS<sub>2</sub>-Reduced Graphene Oxide Composite a High-Capacity, High-Rate, and Long-Cycle Life Sodium-Ion Battery Anode Material. *Adv. Mater.* **2014**, *26*, 3854–3859.
- (26) Hu, R.; Ouyang, Y.; Liang, T.; Tang, X.; Yuan, B.; Liu, J.; Zhang, L.; Yang, L.; Zhu, M. Inhibiting Grain Coarsening and Inducing Oxygen Vacancies: The Roles of Mn in Achieving a Highly Reversible Conversion Reaction and a Long Life SnO<sub>2</sub>–Mn–Graphite Ternary Anode. *Energy Environ. Sci.* 2017, 10, 2017–2029.
- (27) Laruelle, S.; Grugeon, S.; Poizot, P.; Dollé, M.; Dupont, L.; Tarascon, J. M. On the Origin of the Extra Electrochemical Capacity