

## Electronic Supplementary Information (ESI): A High Energy-Density Tin Anode for Rechargeable Magnesium-ion Batteries

### Experimental Methods:

#### i. Fabrication of Sn electrodes:

Sn electrodes were fabricated via a traditional pressed powder film method. Sn nanopowder (< 150 nm particle size) was purchased from Sigma Aldrich and used as-received. Carbon black (EC600-JD) was purchased from Ketjen Black International Inc. and used as-received. Polyvinylidene fluoride (KF 1120 polymer – 12 wt. % PVDF) was the binding agent for the powder films and was purchased from Kureha and also used as-received. Sn powder electrodes were composed of 60 wt. % active material (Sn), 30 wt. % carbon black and 10 wt. % binder. The KF polymer was added to a pre-weighed Thinky cup and diluted by the addition of 1-methyl-2-pyrrolidone (NMP) purchased from Sigma-Aldrich, and subsequently mixed for 3 minutes in a Planetary Centrifugal Mixer (Thinky USA, Inc.). The necessary amount of carbon black was then added to the Thinky cup and mixed for another 3 minutes. The active material was then added to the Thinky cup mixture containing KF polymer and carbon black and mixed for an additional 5 minutes. The powder slurry was coated onto 25 µm thick copper (Cu) foil (Alfa Aesar) using a doctor blade (100 µm film thickness). The coated active material was dried under vacuum at 80 °C for 24 hours and stored in an argon (Ar) filled glove box, prior to use. Final film thickness was pressed to 70 µm via a press roller.

#### ii. Analytical characterization (XRD, SEM and TEM):

As-fabricated Sn, magnesiated Sn and de-magnesiated Mg<sub>2</sub>Sn films were characterized via X-ray diffraction (XRD) to determine crystallinity and the absence of any impurity phases. All XRD characterization was carried out on a Rigaku Smartlab diffractometer by scanning between 20 and 50, 2-Theta degrees at a rate of 1 degree per minute using Cu K $\alpha$  1.54 radiation. Sn and Mg<sub>2</sub>Sn films were referenced to PDF: 00-004-0673 and PDF: 00-006-0190 in the ICDD database, respectively. XRD analysis was also carried out on the as-fabricated and magnesiated Mo<sub>6</sub>S<sub>8</sub> to ensure successful magnesiation. Evidence for the magnesiation was found in the peak shift observed for the spectra from as-fabricated to magnesiated state.<sup>1</sup> The Mo<sub>6</sub>S<sub>8</sub> and magnesiated-Mo<sub>6</sub>S<sub>8</sub> spectra were referenced to PDF: 04-008-2607 and PDF: 04-013-5406 in the ICDD database, respectively.

Field emission scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were utilized to characterize the morphology, homogeneity and composition of the as-fabricated Sn films. A FEI Nova NanoSEM 200 outfitted with an Oxford EDX system, was operated at 5-20 kV, using a spot size of 3-5 and a working distance of 4-5 mm. Specific analysis related to the morphological and compositional differences between the as-fabricated, magnesiated Sn and de-magnesiated Mg<sub>2</sub>Sn films was carried out via transmission electron microscopy (TEM)-EDX. A Philips CM-100 TEM operated at 100 kV, outfitted with an Oxford EDX system and a JEOL 2010 TEM

operated at 200 kV, outfitted with an EDAX EDX system, were utilized for all studies. TEM samples were prepared within an Ar filled glove box to avoid exposure to air.

iii. Electrochemical cycling of anodes:

Initial galvanostatic magnesiation (defined as insertion of  $\text{Mg}^{2+}$ ) / de-magnesiation (defined as extraction of  $\text{Mg}^{2+}$ ) experiments were carried out on the as-fabricated Sn anodes to test their feasibility as insertion-type anodes, and their rate capability. Sn electrodes were tested by cutting out 15 mm diameter ( $1.77 \text{ cm}^2$  area) electrodes from the fabricated Sn powder/Cu foil assembly (as explained in i). The active material loading content was  $0.95 \text{ mg cm}^{-2}$ . Each electrode was tested in a Tomcell (TJ-AC Tomcell Japan<sup>2</sup>) using a 250  $\mu\text{m}$  thick (28 mm diameter) standard glass filter (Sigma-Aldrich) as a separator and 100  $\mu\text{m}$  thick (19 mm diameter) polished magnesium (Mg) foil (ESPI Metals) as the counter electrode. Mg foil was polished by scraping each side of the foil with a standard microscope glass slide and wiping clean with a Kimwipe (Kimberly-Clark) within an Ar filled glove box. The electrolyte (350  $\mu\text{L}$  per cell) used for these tests was 2 mL ethylmagnesium chloride (Sigma-Aldrich), 1 mL diethylaluminum chloride (Sigma-Aldrich) added to 13 mL anhydrous tetrahydrofuran (THF) (Sigma-Aldrich); (EtEt<sub>2</sub>). All Sn electrodes were cycled at various C-rates (0.002C to 0.05C) at 25 °C and compared to the performance obtained from cycling bismuth (Bi) anodes (80 % active material, 10 % carbon black, 10 % binder). Bi anode pressed powder films were prepared using the same procedure as Sn anodes in (i). Bi powder was purchased from Sigma-Aldrich and used as-received. The active material loading content was  $3.16 \text{ mg cm}^{-2}$ . All cells were assembled in an Ar filled glove box to prevent exposure to air.

iv. Full-cell experiments using  $\text{Mo}_6\text{S}_8$ :

Chevrel Phase ( $\text{Mo}_6\text{S}_8$ ) cathodes were fabricated following previously published work.<sup>3</sup> Galvanostatic magnesiation/de-magnesiation of  $\text{Mo}_6\text{S}_8$  experiments were run using a pre-magnesiated Sn ( $\text{Mg}_2\text{Sn}$ ) anode and were carried out in both EtEt<sub>2</sub> (organohaloaluminate) electrolyte (350  $\mu\text{L}$  per cell) and conventional electrolyte (350  $\mu\text{L}$  per cell) – 0.5 M magnesium bis(trifluoromethanesulfonyl)imide –  $\text{Mg}(\text{N}(\text{SO}_2\text{CF}_3)_2)_2$  in 1,2-Dimethoxyethane (DME) (Sigma-Aldrich) in a Tomcell.  $\text{Mg}(\text{N}(\text{SO}_2\text{CF}_3)_2)_2$  was purchased from Kishida Chemicals Co., Ltd. and used as-received (no drying procedure was utilized for this salt). All Sn anodes were chemically pre-magnesiated using the EtEt<sub>2</sub> electrolyte by soaking the Sn pressed powder film with Mg foil (sandwiched together) for 72 hours at 25 °C in an Ar filled glove box, prior to the full-cell experiments. Magnesiated anodes were thoroughly rinsed in THF prior to use and dried in a vacuum oven at 25 °C for 1 hour, to remove excess surface bound electrolyte. The cathode active material loading content was  $1.13 \text{ mg cm}^{-2}$  and the anode active material loading content was  $14.12 \text{ mg cm}^{-2}$  for both cells.

v. Parameters for DFT calculations:

DFT calculations were performed with the Vienna Ab Initio Simulation Package (VASP) using projector augmented wave (PAW) pseudopotentials and exchange-correlation functionals parameterized by Perdew, Burke, and Ernzerhof for the generalized gradient approximation (GGA).<sup>4-7</sup> All ions were fully relaxed, as were the shape and the volume of the supercell. A numerical convergence to 2 meV per atom was ensured by using a cutoff energy of 400.0 eV and an appropriate Gamma centered k-point mesh.

vi. Potentiostatic magnesiation of Mo<sub>6</sub>S<sub>8</sub>:

In order to demonstrate that the full capacity of a Sn anode could be utilized in a Mg-ion battery, two special Mo<sub>6</sub>S<sub>8</sub>/Mg<sub>2</sub>Sn full-cells were fabricated. Due to the unavailability of a suitable high capacity cathode, the loading level of Mo<sub>6</sub>S<sub>8</sub> was increased in these cells (in comparison to iv. above) so its overall theoretical capacity would equal that of Sn (theoretical capacity of Mo<sub>6</sub>S<sub>8</sub> is 128.8 mAh g<sup>-1</sup> and theoretical capacity for Sn is 903.04 mAh g<sup>-1</sup>). The cathode active material loading content was 6.66 mg cm<sup>-2</sup> and the anode active material loading content was 0.95 mg cm<sup>-2</sup> for both cells. This full-cell configuration would allow us to completely extract the Mg<sup>2+</sup> from a Mg<sub>2</sub>Sn anode and insert it into the Mo<sub>6</sub>S<sub>8</sub> cathode. Due to the extremely slow C-rates at which the Mg<sub>2</sub>Sn anode de-magnesiates, a potentiostatic approach was utilized for these cells rather than the traditional galvanostatic approach. The application of + 0.1 V for the duration of 72 hours would provide sufficient overpotential (see Figure 3-inset in manuscript) to execute the de-magnesiation of Mg<sub>2</sub>Sn and the simultaneous magnesiation of Mo<sub>6</sub>S<sub>8</sub>. Both, de-magnesiated Mg<sub>2</sub>Sn and magnesiated Mo<sub>6</sub>S<sub>8</sub> were characterized via XRD by scanning between 20 and 50, 2-Theta degrees at a rate of 0.1 degree per minute using Cu K $\alpha$  1.54 radiation.

References:

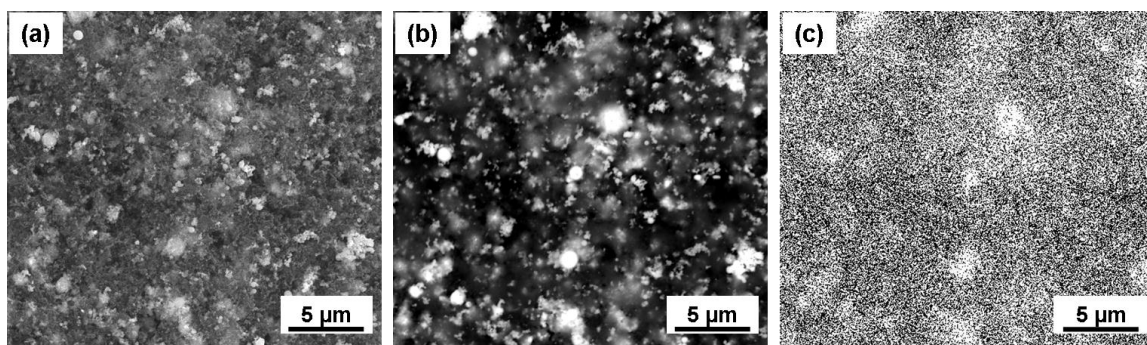
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- 2 *Japan Pat.*, JP 4580751, 2010.
- 3 E. Lancry, E. Levi, A. Mitelman, S. Malovany and D. Aurbach, *J. Solid State Chem.*, 2006, **179**, 1879.
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- 5 P. E. Blochl, *Phys. Rev. B*, 1994, **50**, 17953.
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Additional Results:

vii. SEM characterization:

SEM and SEM-EDX analysis were carried out on the as-fabricated Sn film. The film was imaged and analyzed to determine its surface morphology and the distribution of Sn particles in the electrode. Shown in Figure 1(a) is the SEM image of the as-fabricated Sn film. The distribution of Sn in the powder film is highlighted via the (b) backscattered electron image and (c) EDX map of the Sn film. The areas with high contrast (white) in Figure 1(b) emphasize areas with high Sn content. Despite some areas

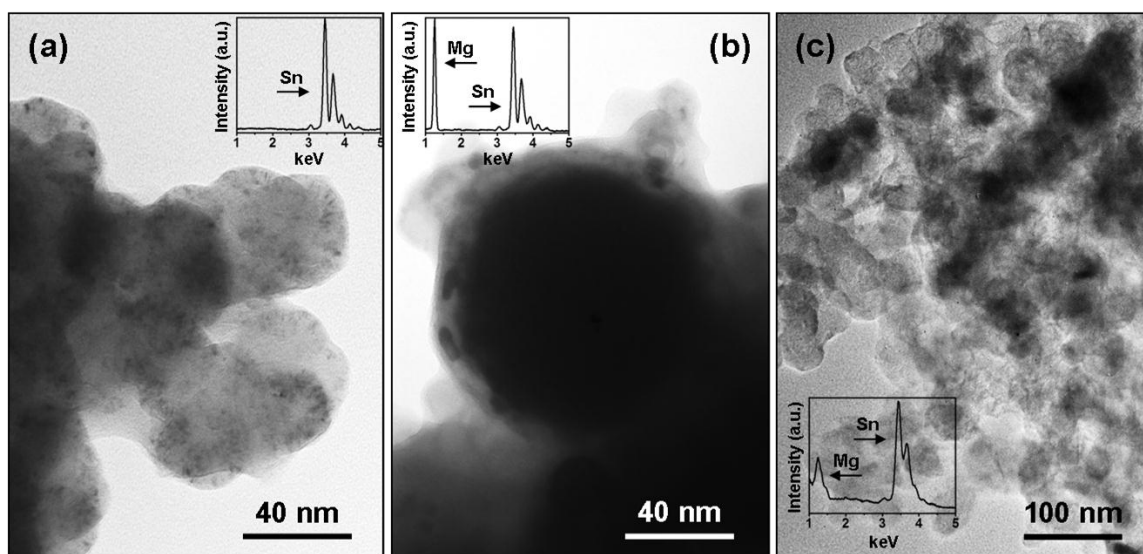
of agglomeration, it is important to note that there is a uniform distribution of Sn throughout the sample as shown by the EDX elemental Sn map in Figure 1(c), where the high contrast spots (white) all signify the presence of Sn.



**Fig. 1** (a) Secondary electron image, (b) backscatter electron image, and (c) EDX map captured of the as-fabricated Sn film.

viii. TEM characterization:

TEM and TEM-EDX analysis were carried out on the as-fabricated Sn, magnesiated Sn ( $\text{Mg}_2\text{Sn}$ ) and de-magnesiated  $\text{Mg}_2\text{Sn}$  films. Figure 2(a) shows a TEM image captured for the as-fabricated Sn anode, (b) shows a TEM image captured for  $\text{Mg}_2\text{Sn}$  and (c) shows a TEM image captured for the de-magnesiated  $\text{Mg}_2\text{Sn}$  anode. Further, TEM-EDX data collected for the  $\text{Mg}_2\text{Sn}$  sample suggested near theoretical elemental ratios between Mg and Sn, while showing significant presence of Mg in the de-magnesiated  $\text{Mg}_2\text{Sn}$  anode. The elemental line spectrum profiles for each sample are provided as insets within each respective TEM image.



**Fig. 2** TEM images and TEM-EDX spectrum profiles (insets) for (a) as-fabricated Sn, (b) magnesiated Sn and (c) de-magnesiated  $\text{Mg}_2\text{Sn}$  films.