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Li deposited on LiCl: An Efficient Reducing Agent

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-Supporting Information-

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General Details. All manipulations were performed under an inert argon atmosphere using standard Schlenk techniques or in a MBraun Unilab glovebox. Solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents. LiCl (99.5+%) was purchased from Fisher Chemical, Lithium granules (99.0+%) were purchased from Acros Organics, Diphenylacetylene (99.0%) was purchased from Alfa Aesar, Dimethyltin dichloride (99.0+%) was purchased from TCI America, Tetramethylsilane (TMS, 99.9+%) was purchased from Sigma-Aldrich, $CDCl_3$ for NMR spectroscopy was purchased from Cambridge Isotope Laboratories and used as received. Multinuclear NMR spectra were recorded on a Bruker 400 MHz spectrometer. Origin Pro 8 was used for the data processing. Scanning electron microscopy (SEM) was recorded on a Tabletop Scanning Electron Microscope TM3030 Plus. An AICOOK blender (Model: NY-8608MA) was used to ground LiCl samples.

For quantitative NMR sample analysis to determine yields: The reactions were quenched at the specified times by the addition of ethanol and the volatiles removed in vacuo to give a crude product which was weighed to +/-0.1 mg (W_1 = total weight of crude). About 10 mg of the crude product was weighed (W_2, accuracy of +/- 0.1 mg) and dissolved in 0.5 mL of $CDCl_3$ measured by a volumetric pipette (containing 4.749 mol/L TMS). Acquiring an ^1H NMR spectrum of the sample and obtaining the integration ratio of the TMS signal (0.0 ppm) to the resonance corresponding the $Sn(CH_3)_2$ protons of 1,1-dimethyl-2,3,4,5-tetraphenylstannole at (0.62 ppm) gaves a value of A which is multiplied by 2 (due to 12 TMS protons and 6 $Sn(CH_3)_2$ protons). The concentration (C in mol/L) of 1,1-dimethyl-2,3,4,5-tetraphenylstannole (from aliquot W_2) in the NMR sample is calculated using following equation:

$$\mathrm{C} = 2 \times A \times 4.749 = 9.498A$$

Therefore, the mole quantity (n in mmol) of stannole in the aliquot W_2 mg can be calculated by following expression:

$$\mathrm{n} = \mathrm{C} \times 0.5 = 0.5\mathrm{C}$$

Substituting in 9.498A for C gives the following formula:

$$\mathrm{n} = 9.498\mathrm{A} \times 0.5 = 4.749\mathrm{A}$$

Thus, the total molar quantity (x in mmol) of 1,1-dimethyl-2,3,4,5-tetraphenylstannole contained in the crude product (W_1) can be obtained using the following equation:

$$x = n \times \frac{W_1}{W_2} = 4.749\mathrm{A}\frac{W_1}{W_2}$$

Since 2.805 mmol of diphenylacetylene was used as the starting material, full conversion of the reaction would generate 1.4025 mmol of 1,1-dimethyl-2,3,4,5-tetraphenylstannole. Thus, the yield (Y) of a specific reaction can be calculated using following equation.

$$\mathrm{Y}\% = \frac{x}{1.4025} \times 100\%$$

Table S1. Schapiro-Wilk test for the weight of lithium granules.

	DF	Statistic	Prob<W
B	714	0.99604	0.06877

Note: at the 0.05 level, the data was significantly drawn from a normally distributed population.

Preparation of Li/LiCl Powder. Lithium chloride was placed in an open vessel in a 135 °C oven for three days. It was then ground to a fine powder by using a 2.1 L, 1450 W household blender for 30 minutes. 40.00 g of the dried LiCl powder was added into a 1.0 L Schlenk flask equipped with a large magnetic stir bar under an argon atmosphere. The powder was then put under dynamic vacuum at 200 °C with stirring for 4 hours. After letting the powder cool to 23 °C, lithium metal (2.00 g) was added and the flask was reheated to 200 °C with constant agitation under an argon atmosphere for approximately one hour. Once the lithium melted, rapid stirring was continued until no bulk metal remained leaving a gray powder of similar visible consistency to the previous lithium chloride. The material was stored in an argon filled glovebox. Yield: 42.00 g (quantitative)

Caution: Elemental lithium can react violently with nitrogen, oxygen, and water to combust. Manipulations are to be conducted in the absence of these (i.e. an argon atmosphere) and be sure that appropriate fire and safety precautions are in place. In conducted experiments with elemental lithium, utilize active stirring to minimize the potential reaction of melted lithium with glassware. The *ca*. 5% w/w Li/LiCl powder is highly hygroscopic, which can combust when exposed to air.

Synthesis of 1,1-dimethyl-2,3,4,5-tetraphenylstannole by Using Li/LiCl Powder. In an argon filled glovebox, diphenylacetylene (500.0 mg, 2.805 mmol), *ca*. 5% w/w Li/LiCl (394.0 mg, 2.805 mmol Li) and a medium-sized stir bar were added to a 50 mL Schlenk flask. Diethyl ether (20 mL) was added to the flask via cannula transfer on a Schlenk line. The reaction mixture was stirred vigorously at room temperature for several hours to give a reddish-brown suspension. The reddish-brown suspension was added to a 50 mL Schlenk flask containing dimethyltin chloride (308.0 mg, 1.403 mmol) in THF (5 mL) via cannula transfer. The combination of both mixtures resulted in a bright yellow solution that was immediately dried under vacuum, the residue was extracted with CH_2Cl_2 (10 mL × 3) and dried to give the crude product. ^{1}H NMR spectroscopy with the crude product in $CDCl_3$ containing 4.749 M TMS was used to quantitatively determine yields.

Synthesis of 1,1-dimethyl-2,3,4,5-tetraphenylstannole Using Li Granules. In an argon filled glovebox, diphenylacetylene (500.0 mg, 2.805 mmol), Li granules (19.5 mg, 2.809 mmol Li) and a medium-sized stir bar were added to a 50 mL Schlenk flask. Diethyl ether (20 mL) was

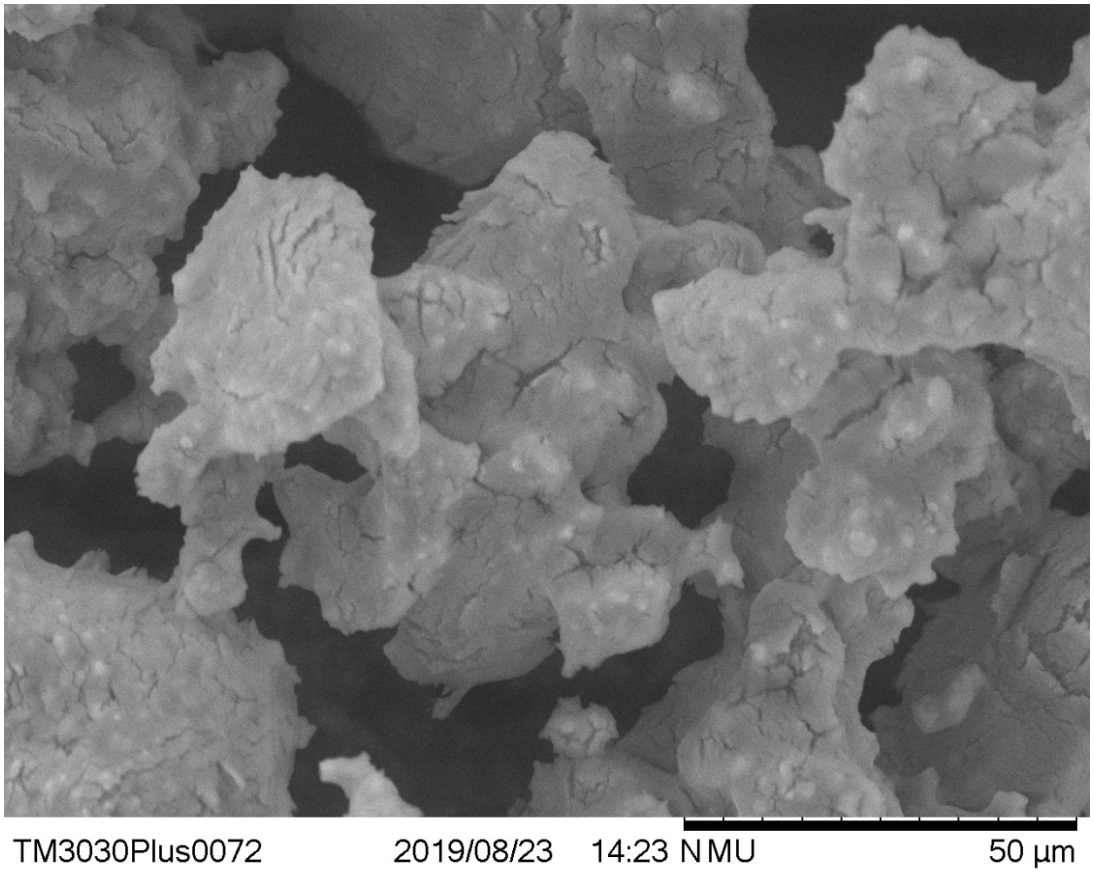
added to the flask via cannula transfer on a Schlenk line. The reaction mixture was stirred vigorously at room temperature for several hours to give a white or brown suspension. The suspension was added to a 50 mL Schlenk flask containing dimethyltin chloride (308.0 mg, 1.403 mmol) in THF (5 mL) via cannula transfer. The combination was immediately dried under vacuum, the residue was extracted with CH_2Cl_2 (10 mL × 3) and dried to give the crude product. ^{1}H NMR spectroscopy with the crude product in $CDCl_3$ containing 4.749 M TMS was used to quantitatively determine yields.

Control Experiments with Li Granules and LiCl added or only LiCl. In an argon filled glovebox, diphenylacetylene (500.0 mg, 2.805 mmol), 394.0 mg of LiCl and a medium-sized stir bar or Li granules (19.5 mg, 2.809 mmol Li), 374.5 mg of LiCl and a medium-sized stir bar were added to a 50 mL Schlenk flask. Diethyl ether (20 mL) was added to the flask via cannula transfer on a Schlenk line. The reaction mixture was stirred vigorously at room temperature for several hours to give a suspension, which was added to a 50 mL Schlenk flask containing dimethyltin chloride (308.0 mg, 1.403 mmol) in THF (5 mL) via cannula transfer. The combination was immediately dried under vacuum, the residue was extracted with CH_2Cl_2 (10 mL × 3) and dried to give the crude product. ^{1}H NMR spectroscopy with the crude product in $CDCl_3$ containing 4.749 M TMS was used to quantitatively determine yields.

Table S2. Reaction yields of stannole with different Li sources.

Lithium Source	Reaction Time (h)	Yield (%)
bare LiCl, no Li^0	20	0
Li granules with 20 fold LiCl by weight	2	5
	18	60
	20	65
Li granules	2	6
	20	63
ca. 5% w/w Li granules deposited on LiCl	2	80

Figure S1. SEM at different sites of bare LiCl powders before grind with 50 μm scale.



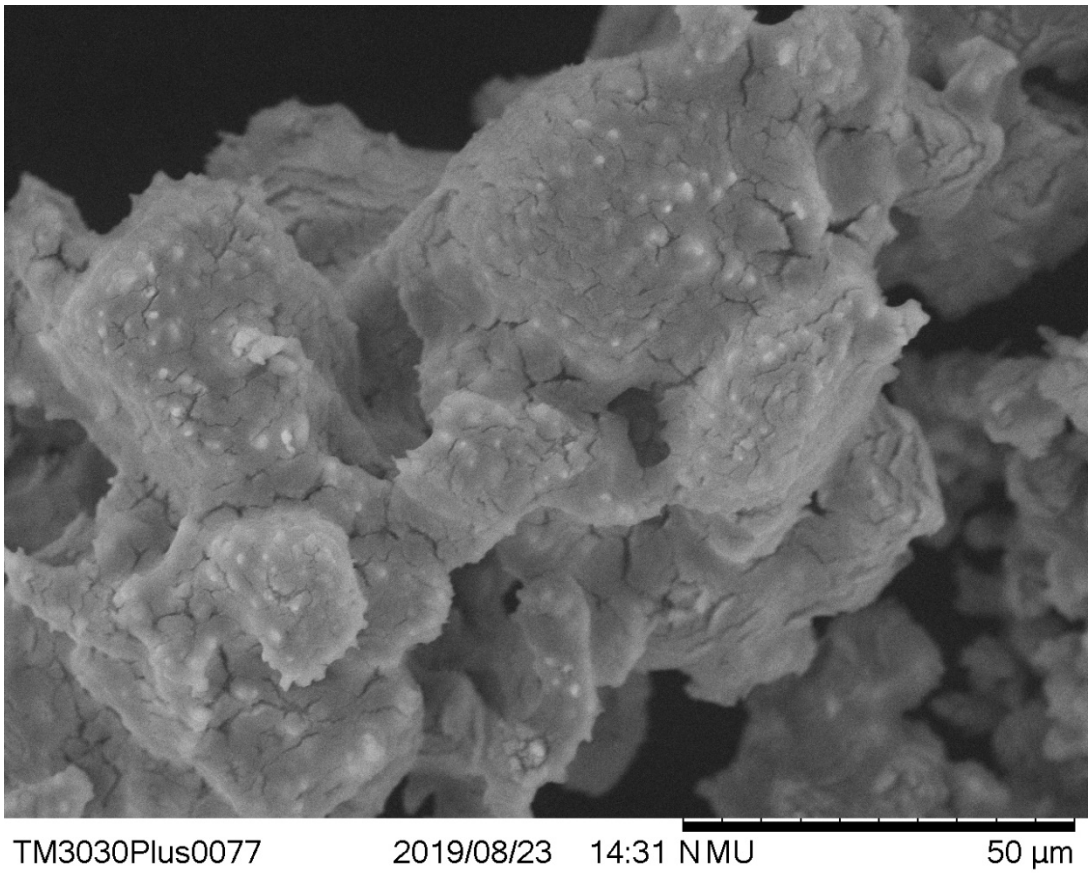
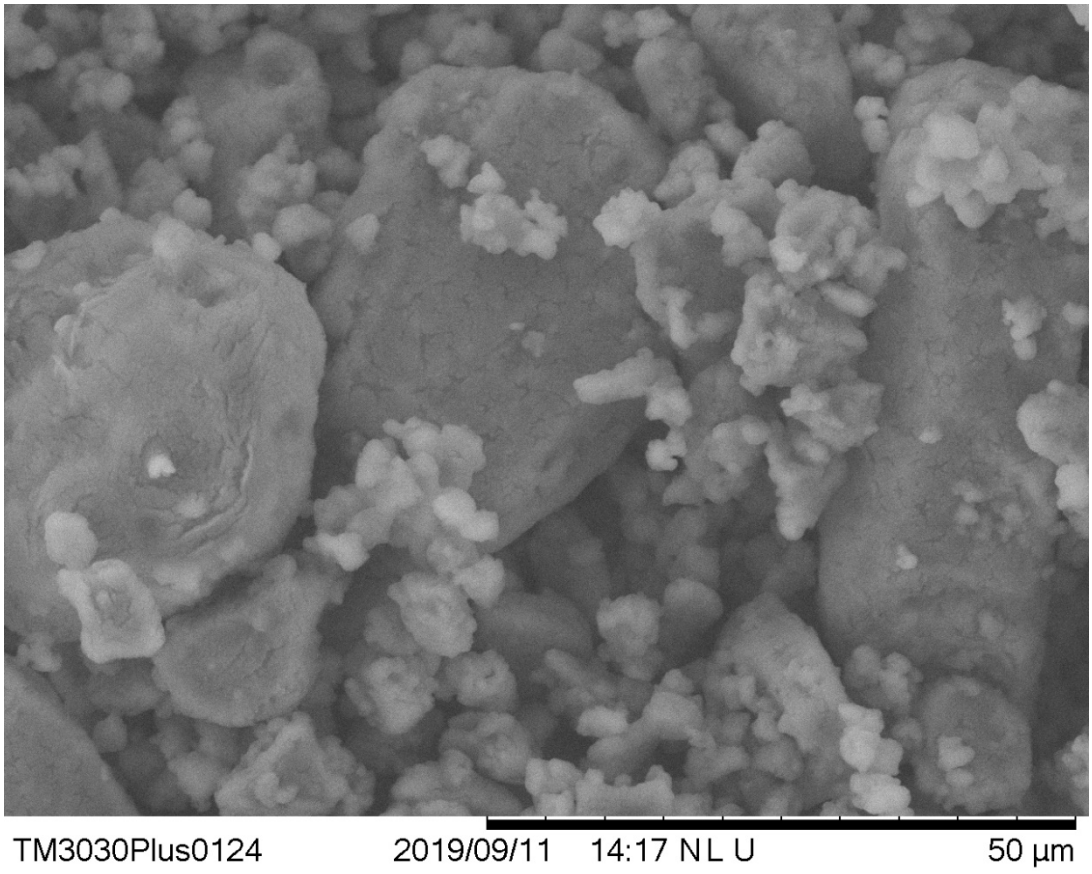


Figure S2. SEM at different sites of bare LiCl powders after grind with 50 μm scale.



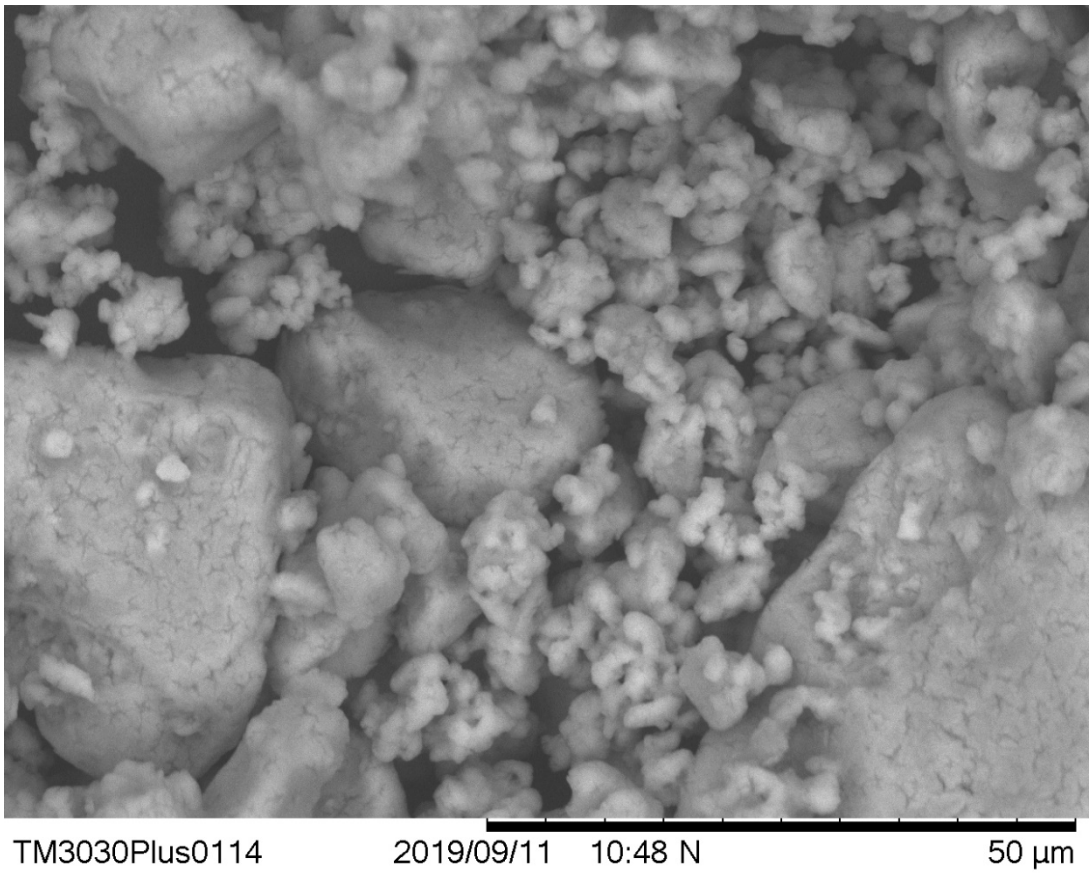


Figure S3. SEM of bare LiCl powders after grind with 20 μm scale.

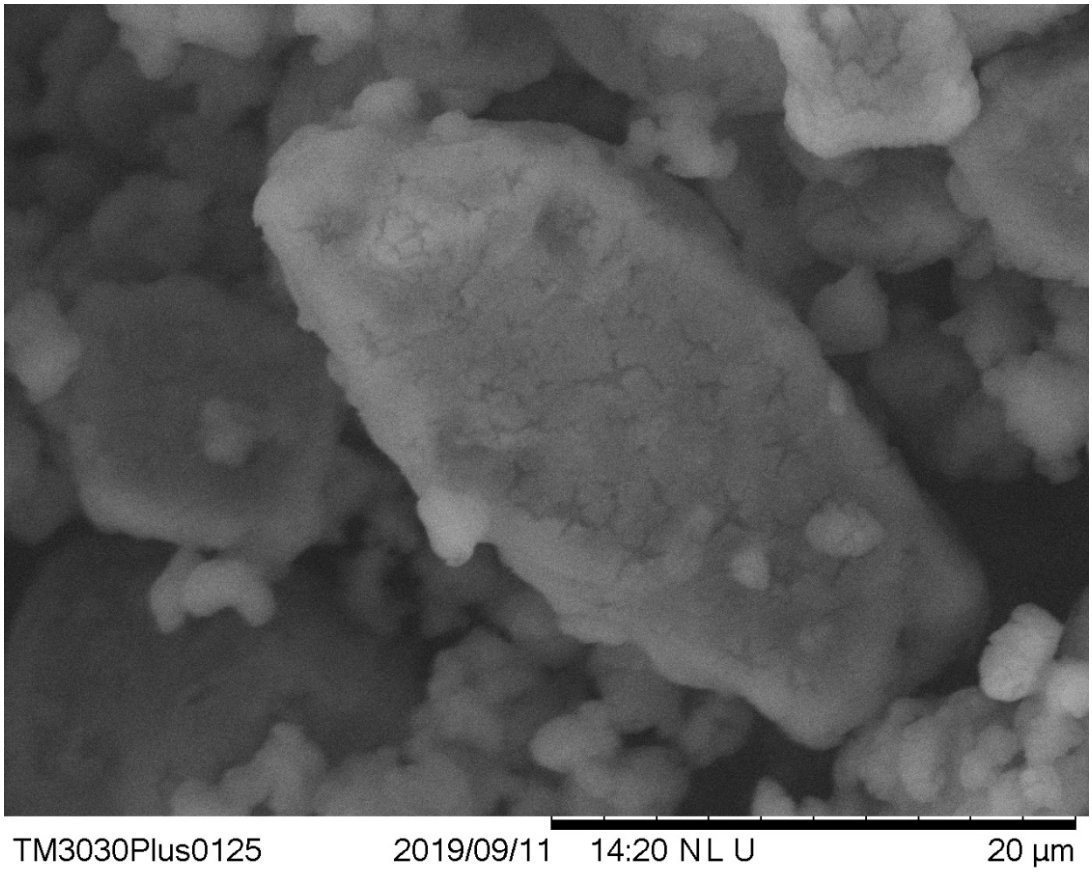
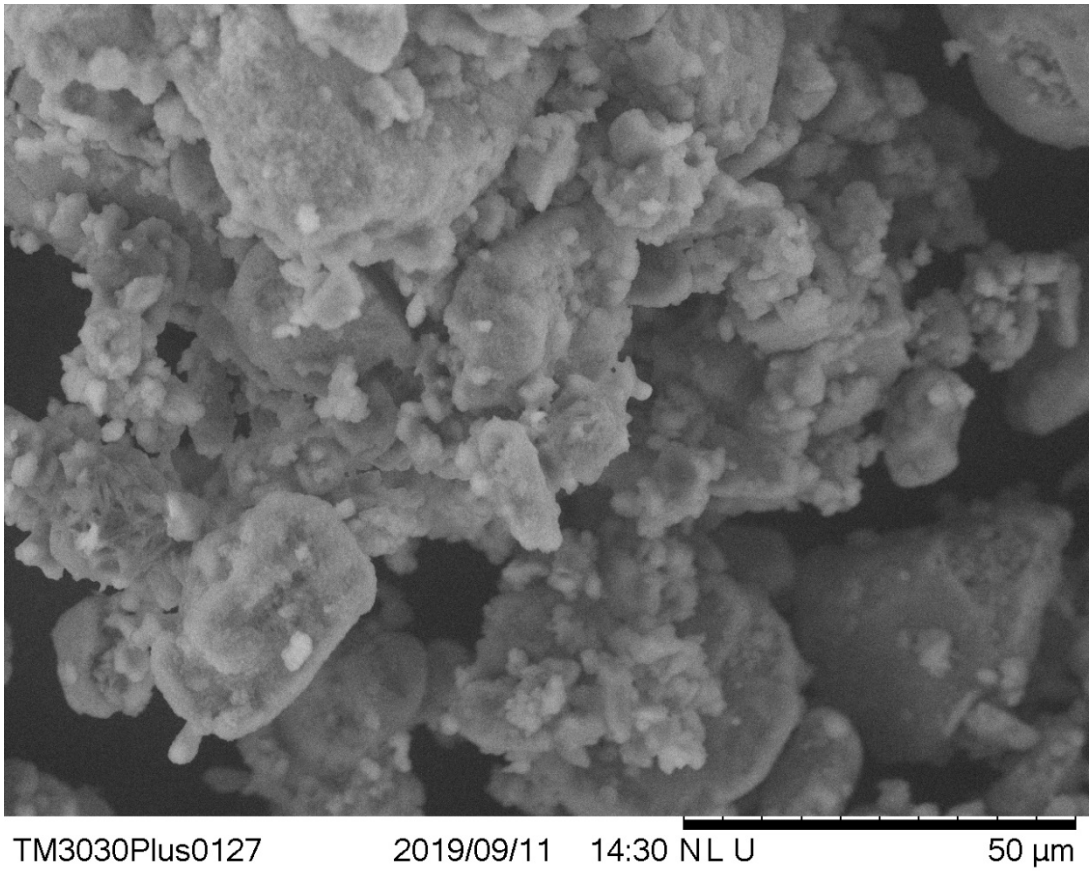


Figure S4. SEM at different sites of *ca*. 5% w/w Li/LiCl powders with 50 μm scale.



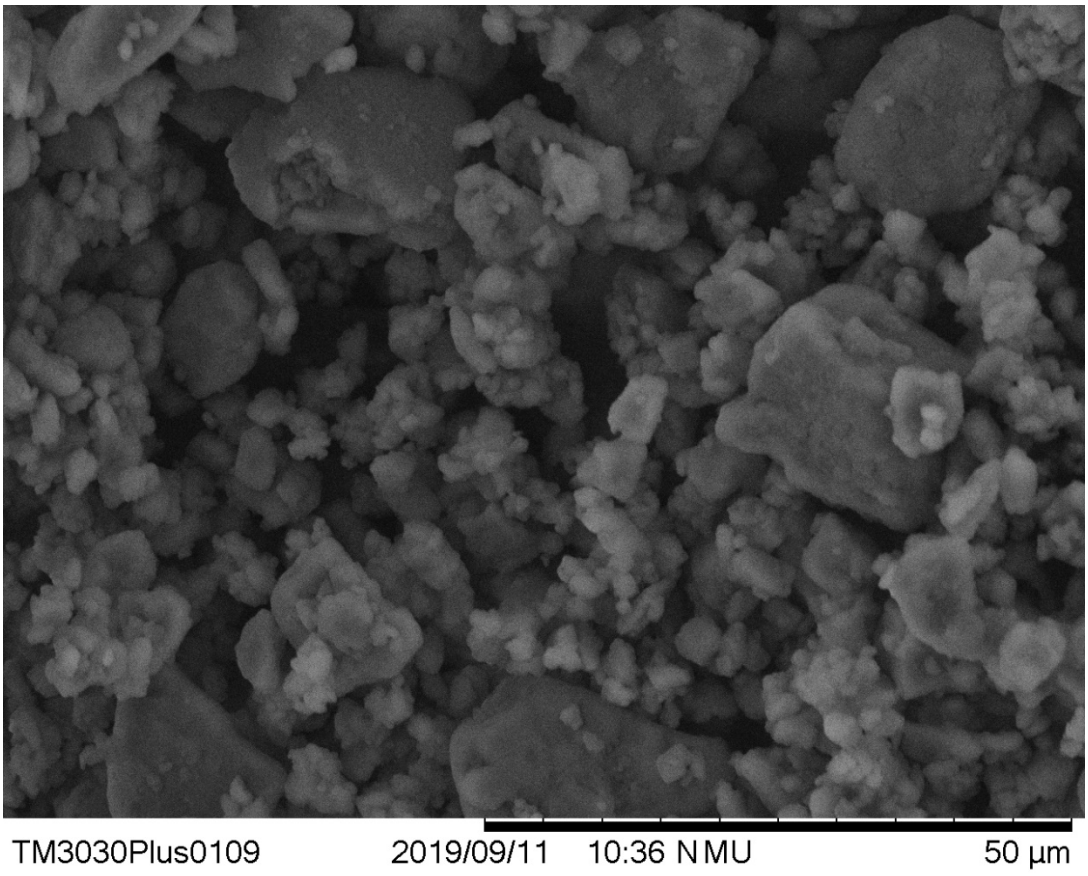


Figure S5. SEM at different sites of *ca*. 5% w/w Li/LiCl powders with 20 μm scale.