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3D $LiMn_2O_4$ thin-film Electrodes for High Rate all solid-state Lithium and Li-ion microbatteries

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Supplementary information

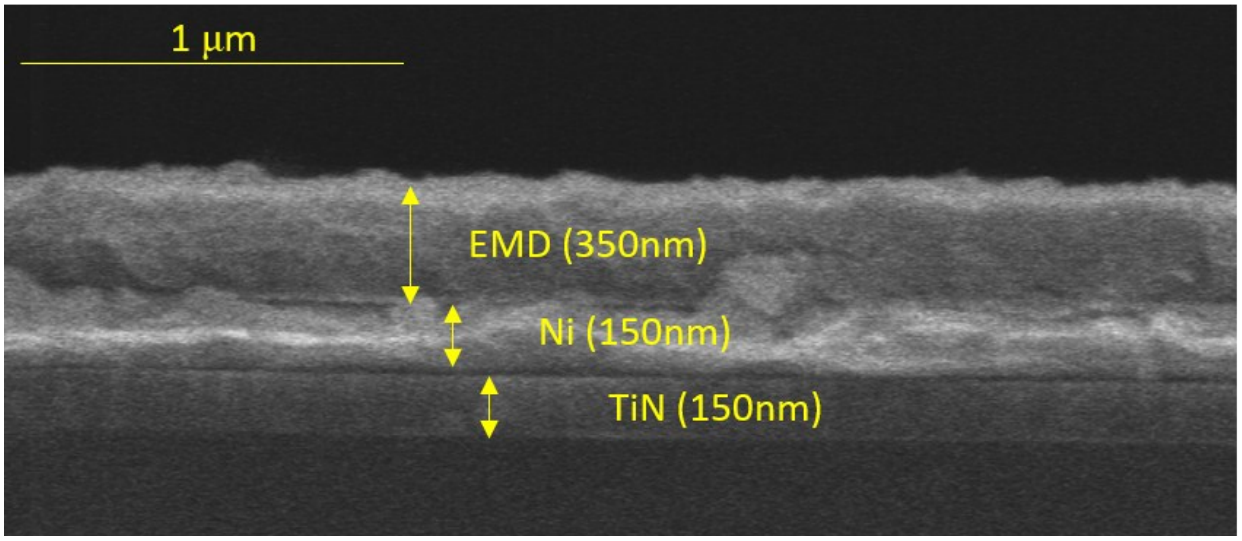

Figure S1: SEM image of a TiN/Ni/EMD sample. The EMD deposition was done at constant current density of 2.5 mA/cm^2 for 1s then 0.5 mA/cm^2 for 200 s. The sample was rinsed in water after deposition then dried at 350 °C for 120 min in air.

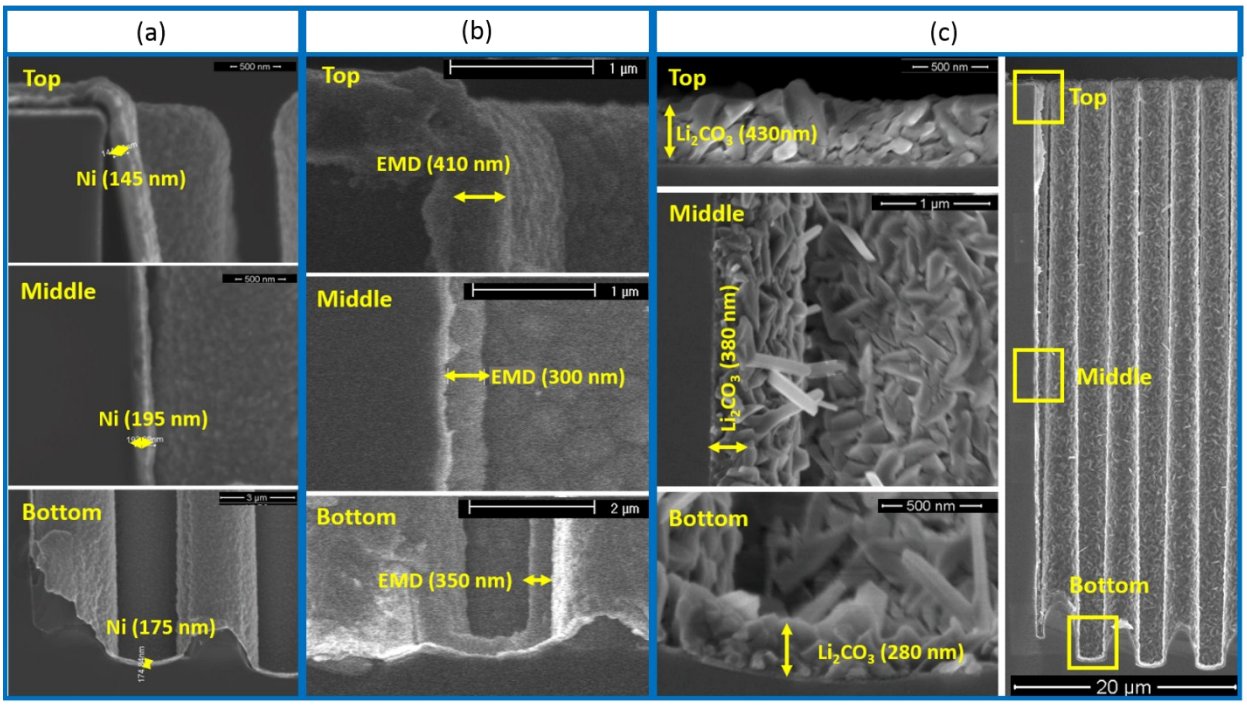

Figure S2. SEM images of: (a) TiN/Ni sample, the Ni film was electroplated on the TiN coated Si microstructured substrate foreseen with a Ni buffer layer (by PVD). (b) EMD on the Ni coated microstructured substrate; (c) Li_2CO_3 deposited by ALD on the TiN coated Si microstructured substrate.

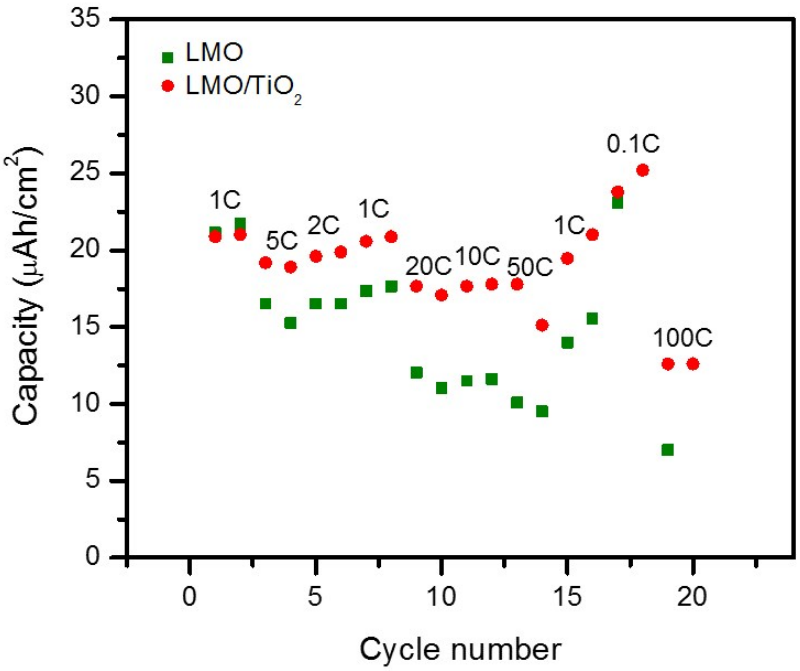

Figure S3. Lithiation capacity densities reached at different C-rates of LMO thin-films when cycled in the [2.4V-4.4V] voltage range. Green squares: bare 420 nm (SEM thickness) LMO thin-film on Ni coated planar substrate. Red dots: 0.5nm TiO_2 coated 420 nm (SEM thickness) LMO thin-film on Ni coated planar substrate.

The rate performance of the LMO thin-film electrode with and without a 0.5nm TiO_2 protective coating is shown in figure S3. For the first cycles at 1C, both the bare and TiO_2 coated LMO thin-film give the same capacity density of 21 μAh/cm^2. The capacity at 1C is kept around the same initial value over cycling in case of usage of TiO_2 protective coating as we excluded the Mn dissolution issue by inhibiting the direct contact between the LMO thin film and the liquid electrolyte. In addition, an improvement of the rate performance of the TiO_2 coated LMO thin film was observed, this can be due to an improvement of the interface contact. More details about the effect of protective coatings on LMO thin films can be found elsewhere.[28]

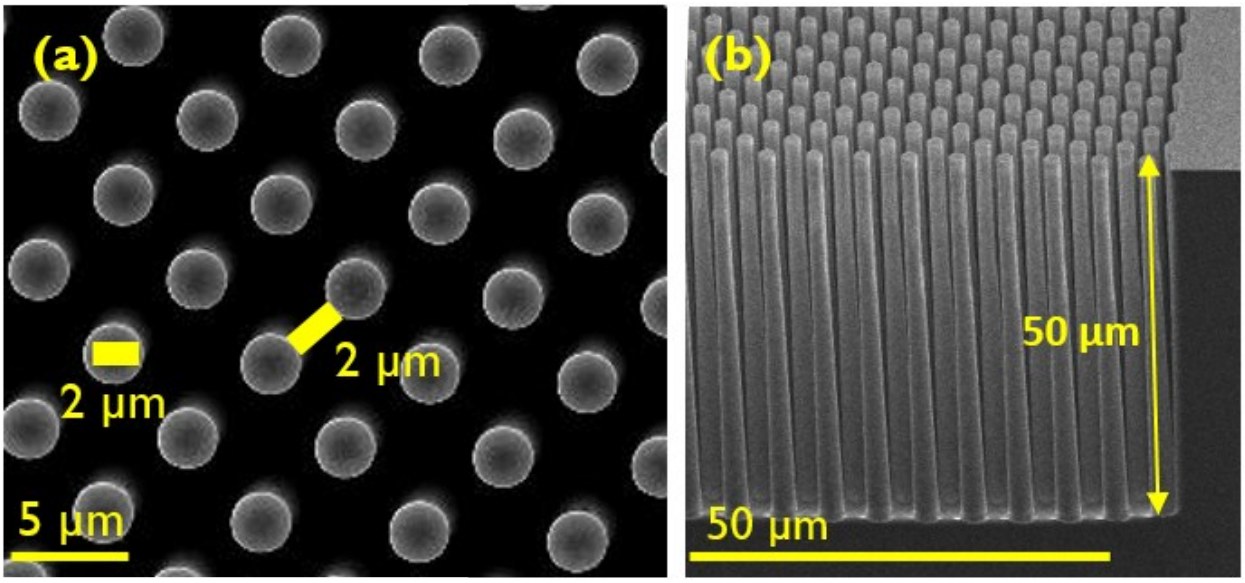

Figure S4. SEM micrographs of the TiN-coated Si micropillar array: (a) Top view of the TiN-coated Si micropillar array. (b) Tilted view of TiN-coated Si micropillar array with a Ni PVD coating.

Table S1: Atomic percentage of the elements in the Li_2CO_3 as determined by ERDA. The Li_2CO_3 was deposited by spincoating on a TiN coated substrate. After spin-coating the sample was annealed on hotplate at 110 °C for 1 min and 280 °C for 2 min.

Element	At. percentage (%)
Li	26.3
C	24.3
O	43.6
H	5.8

Table S2: Summary of the reached lithiation capacities of the LMO sample from different potential ranges ([4.4, 2.4] = full potential range, [4.4, 3.25] = 4V region and [3.25, 2.4] = 3V region) at different c-rates together with the percentage of 4V an 3V regions contributions.

C-rate	Capacity from the 4.4-2.4 V potential range ($\mu Ah/cm^2$)	Capacity from the 4.4-3.25 V potential range ($\mu Ah/cm^2$)	Capacity from the 3.25-2.4 V potential range ($\mu Ah/cm^2$)	% of the 4V region contribution*	% of the 3V region contribution*
0.1	16.52	3.5	13.02	21	79
1	15.53	5.46	10.07	35	65
2	11.79	4.06	7.73	34	66
5	11.79	4.90	6.89	42	58
10	8.26	3.50	4.76	42	58
20	8.61	4.06	4.55	47	53
50	7.14	3.22	3.92	45	55
100	4.90	1.82	3.08	37	63