ALD deposited thin films as model electrodes: a case study of the synergistic effect in Fe_2O_3-SnO2

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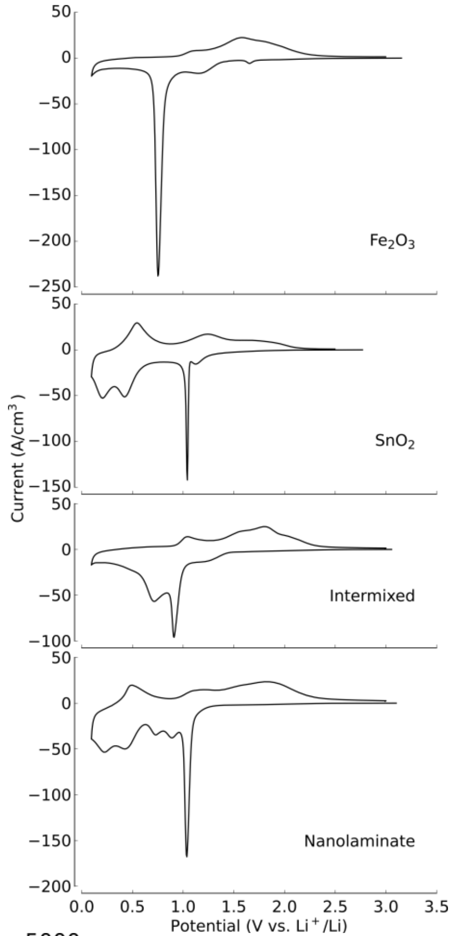
Li-ion batteries are the current state of the art energy storage devices. They have been around since 1991, yet there still is room for improvement. On the anode side, specific capacities are relatively low. High capacity storage mechanisms such as conversion and alloying are gaining attention. However, these reactions impose strain on the material, leading to pulverization, loss of contact, SEI formation and poor kinetics. When two of these materials are combined, a synergistic effect is reported.

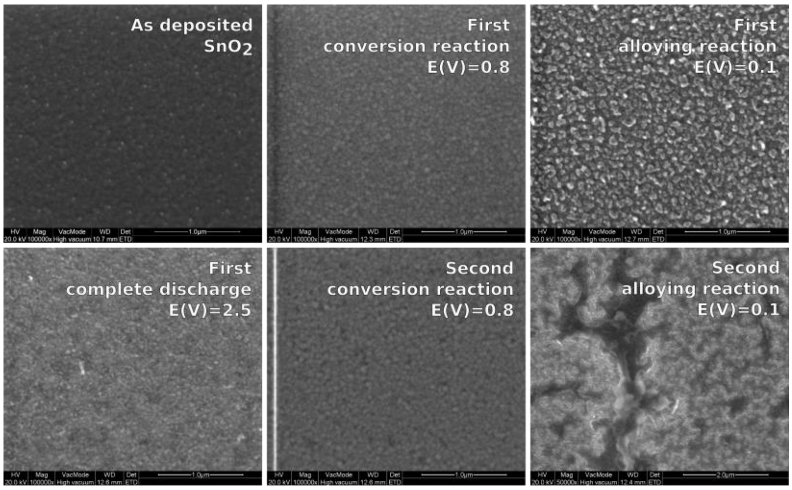
Commercial electrodes are complex systems, so we used atomic layer deposition to deposit our electrodes. Using this method, electrodes could be made without binder nor additive. The digital nature of ALD ensures optimal control over the thickness and stoichiometry of the mixed oxides, and unlike other methods, the degree of mixing of Fe_2O_3 and SnO_2 can be tuned, ranging from mixing at an atomic level, to the deposition of nanolaminates. Here, phase-pure oxides, ternary Fe_2O_3-SnO_2 and nanolaminates were deposited, and studied as anode materials.

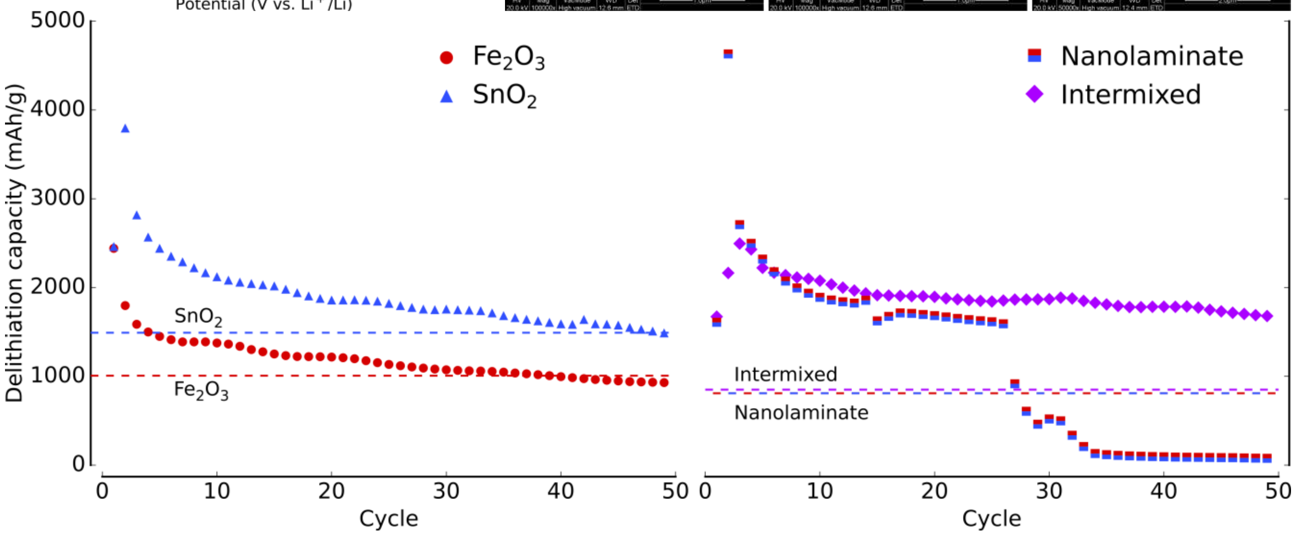
Although alloying of SnO_2 delivers a huge capacity, undesirable island formation occurs. Evaluation of intermixed Fe_2O_3-SnO_2 shows that the conversion of Fe_2O_3 still occurs, yet the conversion and subsequent alloying of SnO_2 is no longer present. Instead, another reaction occurs around 0.9V vs Li^+/Li which has no analogon in either pure SnO_2 or Fe_2O_3. Therefore it is hypothesized that it is a reaction of Li^+ with the Fe_xSn_yO ternary oxide. Although the mix of these oxides shows no alloying of Sn, it ensures a better cycle life of the material, as the island formation caused by the alloying is avoided. This can be seen from the cyclability test, as the capacity of the mixed material fades of less than the SnO_2. From a kinetics point of view, this fully intermixed material performs comparable to the Fe_2O_3, especially at high currents.

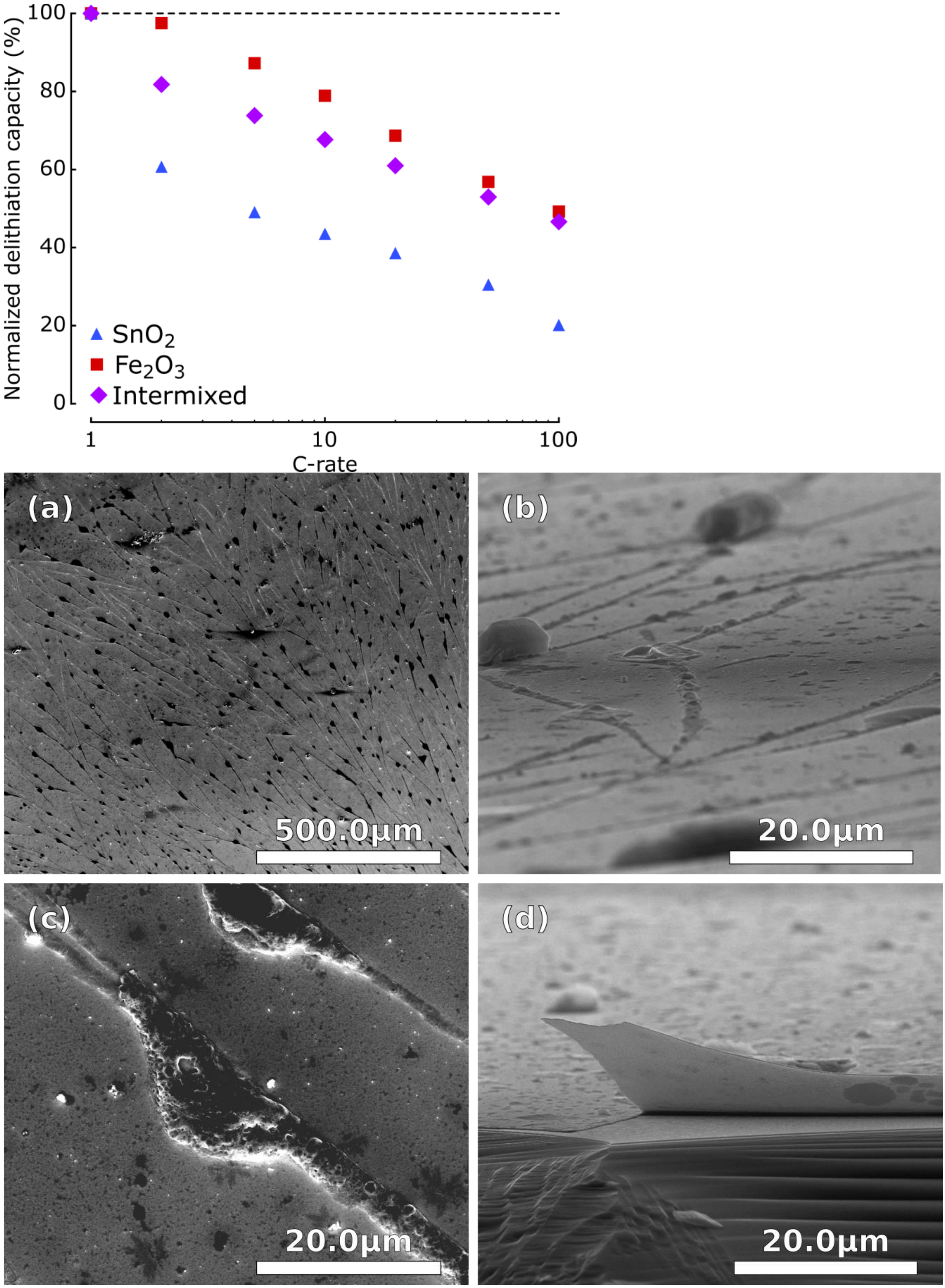
From the CV of the nanolaminate, we can identify all the previous peaks: the interfaces between the oxide layers give rise to the peaks associated with those for the mixed material. The peaks corresponding with the conversion and subsequent alloying of SnO_2 are also clearly present. This entails that although the nanolaminate also provides a large capacity, the alloying of the Sn still occurs and causes great stress and loss of contact. This can be seen from the discrete loss of capacity during cycling and the SEM picture taken after cycling the nanolaminate for a mere 50 cycles.

In conclusion, we used ALD to prove that in order to maximize the synergistic effect between Fe_2O_3 and SnO_2, an atomically mixed material is preferred over a system containing sharp interfaces between the oxides.


Current (A/cm^3)
Potential (V vs. Li$^+$/Li)
Fe_2O_3
SnO_2
Intermixed
Nanolaminate


As deposited SnO_2
First conversion reaction E(V)=0.8
First alloying reaction E(V)=0.1
First complete discharge E(V)=2.5
Second conversion reaction E(V)=0.8
Second alloying reaction E(V)=0.1


Delithiation capacity (mAh/g)
Cycle
Fe_2O_3
SnO_2
Nanolaminate
Intermixed



Normalized delithiation capacity (%)
100
80
60
40
20
0
1
10
100
C-rate
SnO2
Fe2O3
Intermixed
(a)
500.0µm
(b)
20.0µm
(c)
20.0µm
(d)
20.0µm