Experimental Visualization of Commercial Lithium Ion Battery Cathodes: Distinguishing Between the Microstructure Components Using Atomic Force Microscopy

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Supporting Information

1. DETERMINATION OF CATHODE CHEMISTRIES

1.1 Cathode 1:

Cathode 1: SEM Analysis

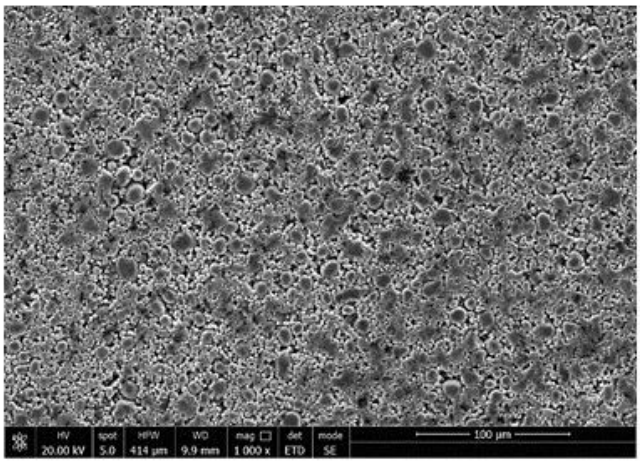

Figure S1. SEM image of the cathode from cell A. EDX analysis was carried out on the entire image area to achieve a 'bulk' elemental composition.

Table S1. EDX Analysis on Cell A, Taken across the Entire Image Area in Figure 1

Element	Weight %	Atomic %
C	21.59	40.07
O	26.34	36.70
F	3.80	4.46
Al	0.22	0.18
Mn	14.15	5.74
Co	11.98	4.53
Ni	21.92	8.32
Total	100.00	100.00

The EDX data for cell A shows the presence of nickel, manganese and cobalt, suggesting the active material is lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$, NMC). The atomic percentages of each transition metal suggest the closest version of NMC is NMC-532 ($LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$). The presence of fluorine in the spectrum also indicates that the binder is likely to be polyvinylidene fluoride (PVDF).

1.2 **Cathode 2:**

Cathode 2: SEM Analysis

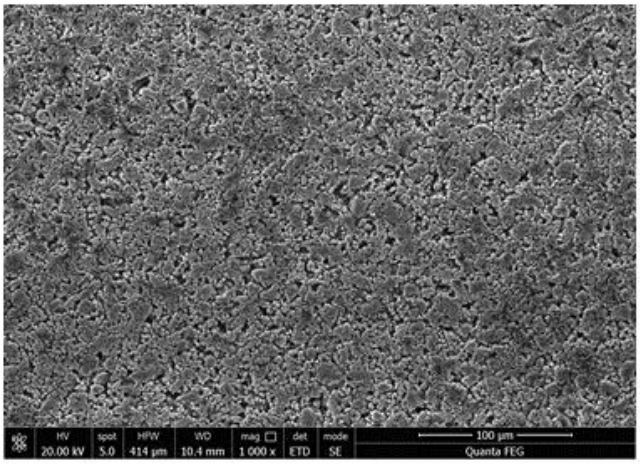

Figure S2. SEM image of the cathode from cell B. EDX analysis was carried out on the entire image area to achieve a 'bulk' elemental composition.

Table S2. EDX Analysis on Cell B, Taken across the Entire Image Area in Figure 2

Element	Weight %	Atomic %
C	14.36	24.37
O	48.80	62.18
Mn	27.48	10.20
Co	1.05	0.36
Ni	8.32	2.89
Total	100.00	100.00

The EDX data in table 2 increase in the atomic percentage of manganese compared to cell A, suggesting the two cathodes have different active material chemistries. Further investigation using EDX mapping shows that particles can be distinguished from each other by their transition metal content. Some particles show all 3 metals (Ni, Mn and Co) present and are some form of NMC. Others show just Mn present, these are some form of manganese oxide,

most likely the spinel Mn_2O_4. While cell A and B contain different cathode active material chemistries, this is not so important for this study as we are determining contrast between soft polymer and hard active particles. The key interest is in the size and shape of the particles.

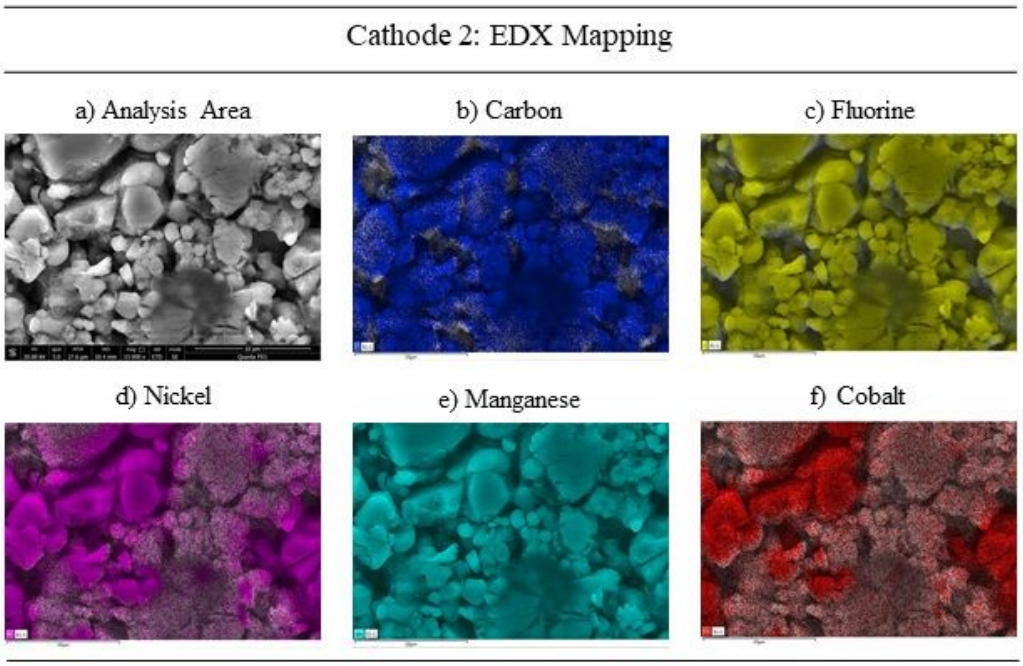

Figure S3. EDX mapping images of cell B showing; a) the analysis area, b) the carbon overlay, c) fluorine overlay, d) nickel overlay, e) manganese overlay, f) cobalt overlay. The mapping shows chemical differences between particles, suggesting there are two different kinds of active material chemistries present.

1.3 Cathode 3:

Cathode 3 was extracted from a used EV. The chemistry is the same as for cathode 2. SEM was used to confirm this and is shown in figure 4 and table 3. Spectrum 1 shows high nickel and cobalt content, suggesting it is some form of NMC. Spectrums 2 and 3 shows large amounts of

manganese, indicating it is likely a manganese oxide. Spectrum 4 is of a large clump of binder, which likely contains a high amount of conductive carbon additive.

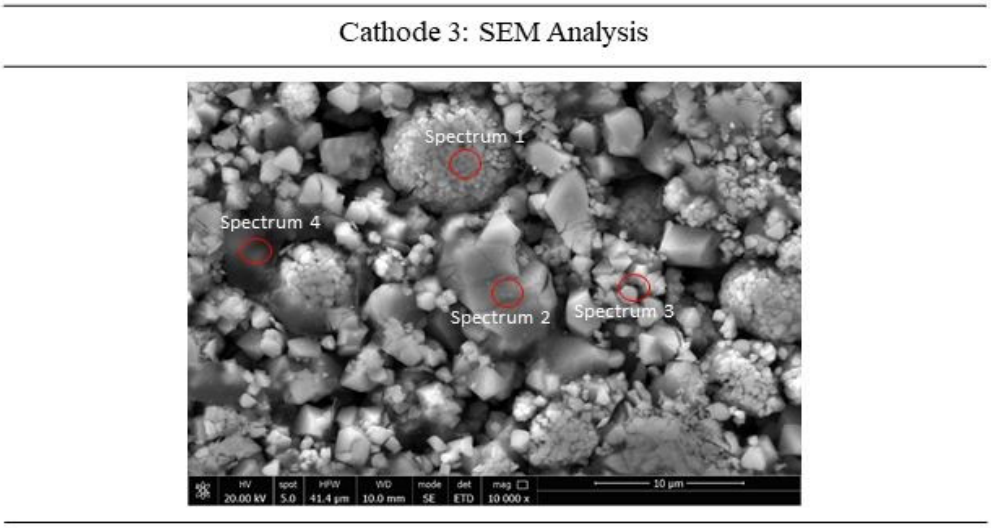

Figure S4. SEM image of cathode 3 at 10,000x magnification. Multiple EDX spectrums were recorded at different locations in order to confirm that the cathode chemistry was the same as cell 2.

Table S3. EDX Information for the 4 Spectrums Recorded on Cathode 3
Spectrum locations are shown in Figure 4.

Spectrum 1			Spectrum 2	
Element	Atomic %		Element	Atomic %
C	15.39		C	16.73
O	52.33		O	53.64
F	1.89		F	3.60
Al	1.58		Al	0.36
Mn	1.93		Mn	24.78
Co	4.31		Co	0.58
Ni	22.57		Ni	0.31
Total	100.00		Total	100.00
Spectrum 3			Spectrum 4	
Element	Atomic %		Element	Atomic %
C	22.92		C	74.84
O	50.50		O	14.06
F	5.11		F	2.21
Al	0.71		Al	0.16
Mn	19.94		Mn	8.11
Co	0.48		Co	0.21
Ni	0.35		Ni	0.42
Total	100.00		Total	100.00

1.4 DSC Analysis:

DSC Analysis has been used to confirm the polymer binder in the cathode composites. A Mettler Toledo DSC1 with STARe software was used to run these tests. Figure 5 shows DSC plots for all 3 cathodes, all exhibit a characteristic peak at ~170 °C which is the melting peak for polyvinylidene fluoride (PVDF).

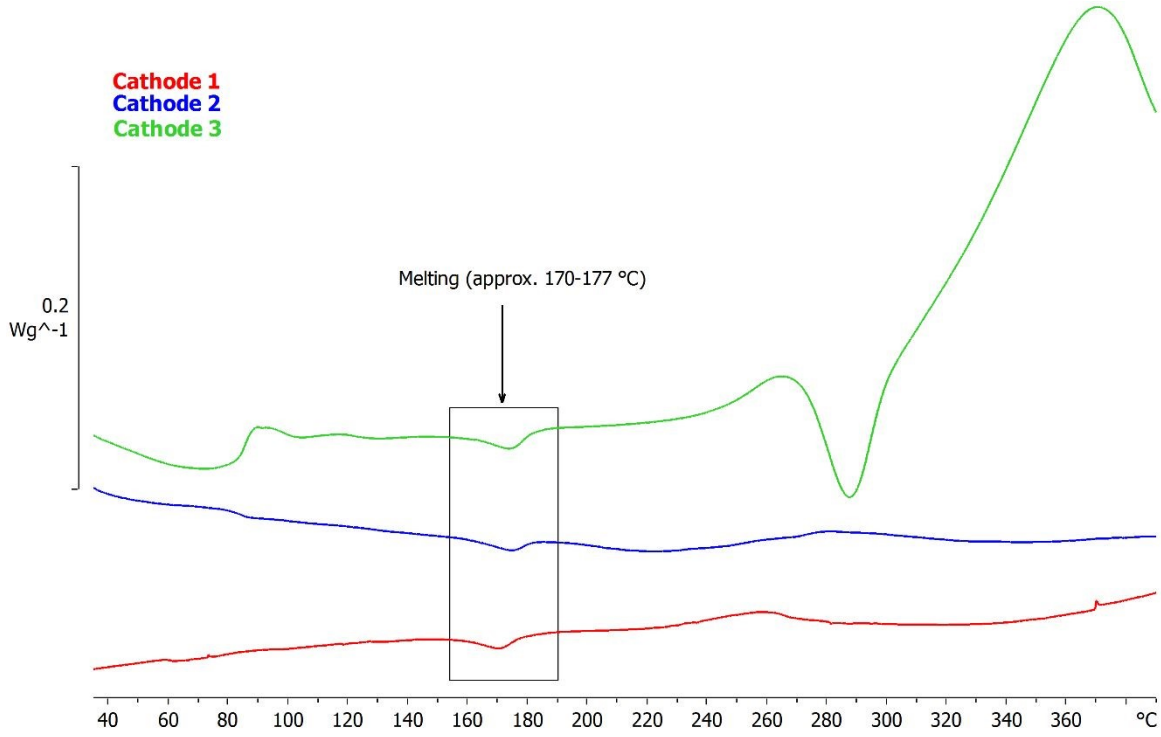

Figure S5. DSC plots for cathodes 1, 2 and 3. All 3 cathodes show a characteristic peak (shown in the black box) between 170 °C and 177 °C which is the PVDF melting point.

2. CONSIDERATIONS FOR PEAK FORCE QNM

Since Peak Force QNM gives quantitative information about the materials studied, the models used to calculate the modulus and the variations that may affect its value must be considered. The model used in this report is the Sneddon model, one that assumes a conical indenter, where the modulus is calculated using the half angle of the cone and the indentation depth. The alternative to the Sneddon model is the DMT model, which assumes a spherical point of a known radius indenting the substrate. Figure 6 shows schematics representing the two indentation models.

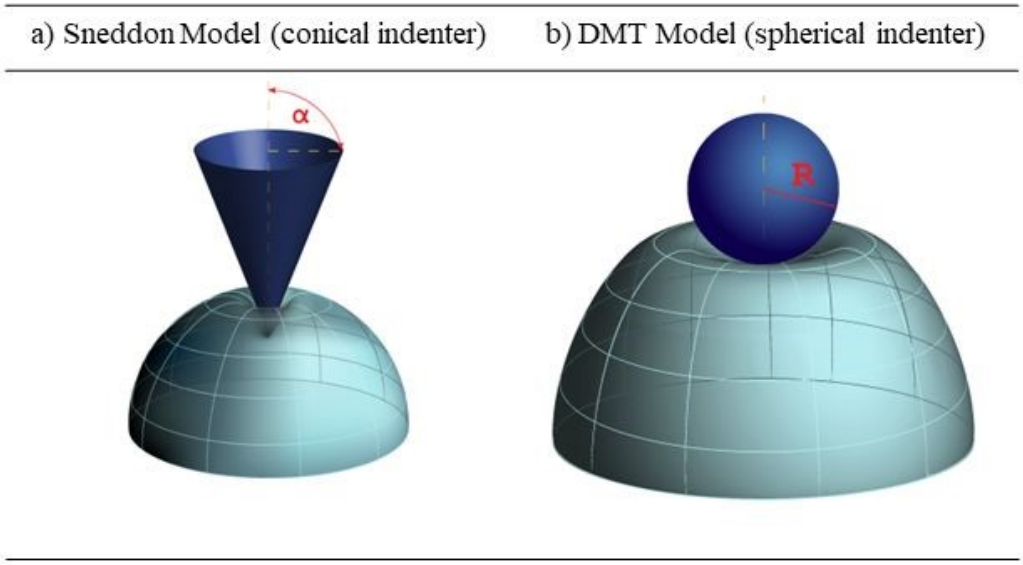

Figure S6. Diagrams representing the two possible indentation mechanisms that can be utilized to determine the sample modulus; a) the Sneddon model utilizes the half angle of the cone while b) the DMT model utilizes the radius of a spherical point.

In order to achieve some deformation of the rigid active material of the cathodes, the stiff cantilever of the RTESPA-525 probe was used (200 N m^{-1} spring constant). This probe is produced with a sharp, non-spherical tip ('radius' of ~8 nm) and so we have decided that the Sneddon model would be most closely related to what is happening. Testing the two models on both a cathode and a reference sample shows that quantitative information differs between

the two models. Figure 7 shows the DMT and Sneddon modulus mappings of cathode 2 and a film of polystyrene (PS) with particles of low-density polyethylene (LDPE), this sample is provided with the Peak Force QNM kit by Bruker. Other considerations about the quantitative analysis of these samples using this technique include:

- The samples are relatively rough compared to most samples studied using this technique, which are normally thin films.
- The roughness means a high setpoint of 400 nN is therefore required to track the surface well and allow for some deformation of the hard sample.
- By pressing into the hard sample with forces such as these, damage to the tip is very likely, changing the tip-sample contact area and so the absolute modulus values become less reliable.
- The reported Young's modulus of LCO and NMC materials are ~200 GPa as reported in the main text, these values are suggested by Bruker to be too high for QNM to reliably measure.
- The difference in Young's modulus between the active particles and PVDF is very high, and so accurately measuring the modulus of both materials is not trivial.

Therefore, rather than use this technique as assessing the absolute Young's modulus values, in this case it should be used in a more qualitative manner, where the contrast in the modulus mappings are the source of analysis and the values are compared relative to each other.

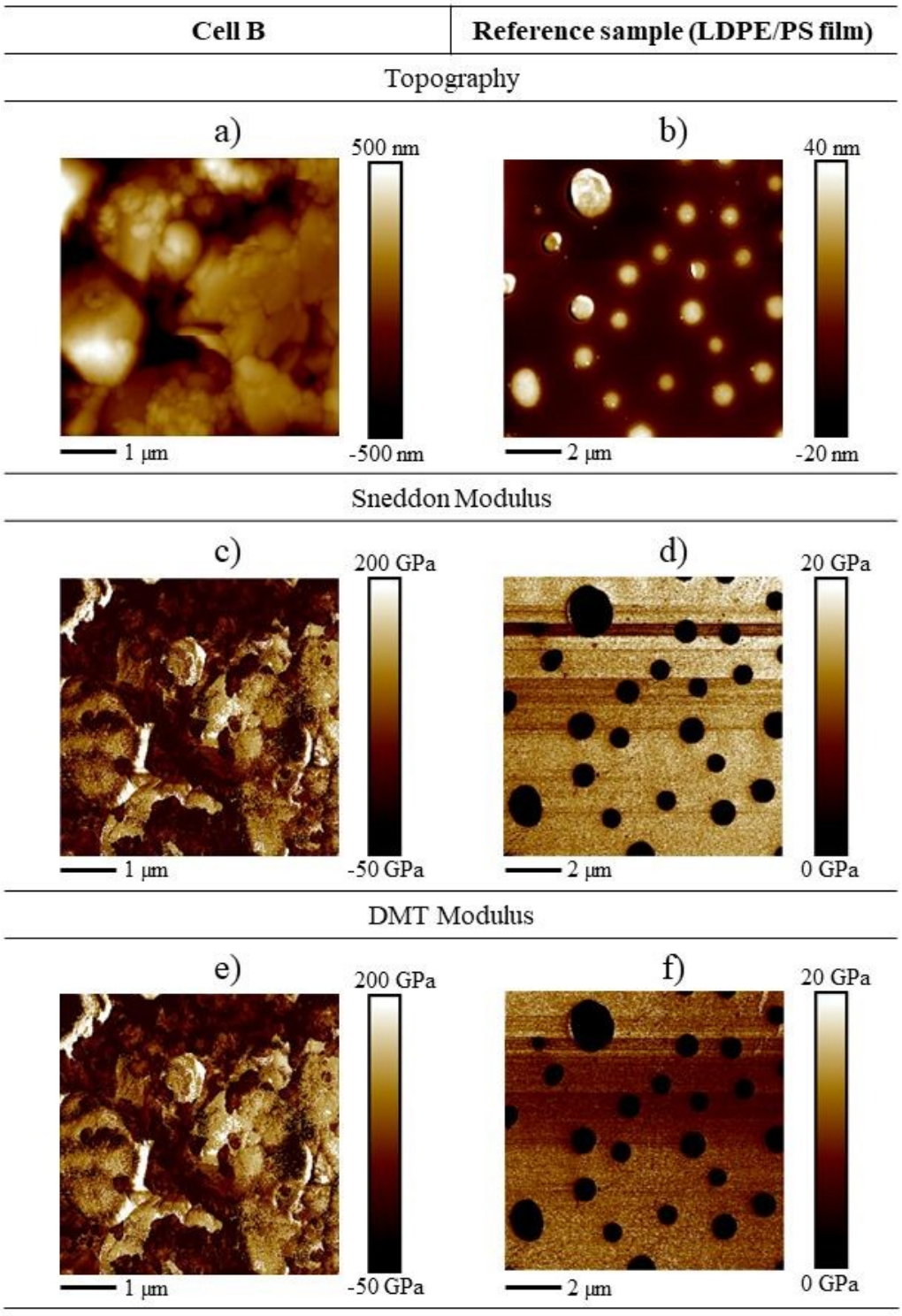

Figure S7. Topography and modulus images of cell B and the reference sample. Mappings using the Sneddon model, c) and d), can be compared with the DMT model, e) and f). Cell B was imaged with imaged with a RTESPA-525 probe (200 N m^{-1}), and the reference sample was imaged with a RTESPA-150 probe (5 N m^{-1} spring constant).