Supplementary Information for “Characterization of Surface Free Energy of Composite Electrodes for Lithium-Ion Batteries”

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Figure S1. (a)-(d) Wenzel model and Cassie-Baxter model for lyophobic and lyophilic surfaces, respectively, and (e) the relationship between $\cos \theta^*$ and $\cos \theta$.
Table S1. Materials used in electrode fabrication.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2 (NMC532)</td>
<td>TODA America, Battle Creek, MI, USA</td>
</tr>
<tr>
<td>A12 graphite (A12)</td>
<td>ConocoPhillips, Houston, TX, USA</td>
</tr>
<tr>
<td>N-Methylpyrrolidone (NMP)</td>
<td>Sigma-Aldrich, St. Louis, MO, USA</td>
</tr>
<tr>
<td>Denka carbon black (Denka CB)</td>
<td>Denka, Tokyo, Japan</td>
</tr>
<tr>
<td>C-NERGY Super C65 carbon black (C65 CB)</td>
<td>Imerys Graphite &amp; Carbon, Bodio, Switzerland</td>
</tr>
<tr>
<td>Carboxymethyl cellulose (CMC)</td>
<td>Sigma-Aldrich, St. Louis, MO, USA</td>
</tr>
<tr>
<td>Styrene-butadiene rubber (SBR)</td>
<td>Targray, Kirkland, Canada</td>
</tr>
<tr>
<td>Solef® XPH-859 (PVDF latex)</td>
<td>Solvay S.A., Brussels, Belgium</td>
</tr>
<tr>
<td>Solef® 5130 (5130 PVDF)</td>
<td>Solvay S.A., Brussels, Belgium</td>
</tr>
<tr>
<td>Kureha w#9300 (9300 PVDF)</td>
<td>Kureha America, New York, NY, USA</td>
</tr>
</tbody>
</table>

Table S2. Surface tension of probe liquids as measured.

<table>
<thead>
<tr>
<th>Probe Liquid</th>
<th>θ_{PTFE} (°)</th>
<th>γ_{lv} (mN/m)</th>
<th>γ_{lv}^a (mN/m)</th>
<th>γ_{lv}^p (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene Carbonate (PL1)</td>
<td>88.03 ± 0.94</td>
<td>41.47 ± 0.13</td>
<td>25.55 ± 0.91</td>
<td>15.91 ± 0.78</td>
</tr>
<tr>
<td>Nicotinyl Alcohol (PL2)</td>
<td>97.26 ± 1.81</td>
<td>50.78 ± 0.27</td>
<td>27.34 ± 2.24</td>
<td>23.45 ± 1.98</td>
</tr>
<tr>
<td>Dimethyl Sulfoxide (PL3)</td>
<td>87.50 ± 0.40</td>
<td>46.48 ± 0.14</td>
<td>32.78 ± 0.73</td>
<td>13.77 ± 0.52</td>
</tr>
</tbody>
</table>

Figure S2. Representative images of the static contact angles between probe liquids and PTFE surface.
Figure S3. The atomic percentage of the elements C, F, O, Li, Mn, Ni, and Co from XPS spectra of the electrode samples.

Figure S4. Representative AFM topographical images of electrode surfaces for Sample 1 to Sample 8.
Figure S5. (a) Representative SP measurements with tip radius of 12.5 μm for Sample 1 to Sample 8.
Figure S5. (b) Representative SP measurements with tip radius of 700 nm for Sample 1 to Sample 8.
Table S3. Apparent SFE of the fabricated electrode samples.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Electrode</th>
<th>$\gamma_{sv}$ (mN/m)</th>
<th>$\gamma_{sv}^* \alpha$ (mN/m)</th>
<th>$\gamma_{sv}^* \beta$ (mN/m)</th>
<th>Convergence Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NMC532-NMP</td>
<td>46.39</td>
<td>19.92</td>
<td>26.47</td>
<td>0.81</td>
</tr>
<tr>
<td>2</td>
<td>NMC532-Water</td>
<td>46.02</td>
<td>19.79</td>
<td>26.23</td>
<td>0.81</td>
</tr>
<tr>
<td>3</td>
<td>A12-NMP</td>
<td>42.42</td>
<td>23.45</td>
<td>18.97</td>
<td>0.81</td>
</tr>
<tr>
<td>4</td>
<td>A12-Water</td>
<td>45.07</td>
<td>21.07</td>
<td>24.00</td>
<td>0.80</td>
</tr>
<tr>
<td>5</td>
<td>NMC532-NMP</td>
<td>46.56</td>
<td>19.98</td>
<td>26.58</td>
<td>0.81</td>
</tr>
<tr>
<td>6</td>
<td>NMC532-Water</td>
<td>43.92</td>
<td>20.49</td>
<td>23.43</td>
<td>0.82</td>
</tr>
<tr>
<td>7</td>
<td>NMC532-NMP</td>
<td>44.15</td>
<td>21.20</td>
<td>22.96</td>
<td>0.80</td>
</tr>
<tr>
<td>8</td>
<td>NMC532-NMP</td>
<td>41.13</td>
<td>23.45</td>
<td>17.68</td>
<td>0.82</td>
</tr>
<tr>
<td>9</td>
<td>NMC532-Water</td>
<td>46.09</td>
<td>19.04</td>
<td>27.05</td>
<td>0.81</td>
</tr>
<tr>
<td>10</td>
<td>A12-NMP</td>
<td>40.11</td>
<td>19.47</td>
<td>20.64</td>
<td>0.81</td>
</tr>
<tr>
<td>11</td>
<td>A12-Water</td>
<td>37.94</td>
<td>22.19</td>
<td>15.75</td>
<td>0.87</td>
</tr>
</tbody>
</table>
MATLAB Codes for Surface Solid Fraction Determination

Example 1: Solve the case of Sample 4 and Sample 11. Both made of A12-Water

% Initial conditions for solid fraction of the two samples
f1 = 1; % Uncalendered surface
f2 = 1; % Calendered surface

% **** Contact angles with probe liquid: Propylene Carbonate **************
theta1_PC = 14.99;  % Sample 4
theta2_PC = 31.48;  % Sample 11
Theta_PC = [theta1_PC, theta2_PC];
Cos_th_PC = cos(Theta_PC.*(pi/180));

% **** Contact angles with probe liquid: Dimethyl Sulfoxide **************
theta1_DMSO = 16.73;  % Sample 4
theta2_DMSO = 34.80;  % Sample 11
Theta_DMSO = [theta1_DMSO, theta2_DMSO];
Cos_th_DMSO = cos(Theta_DMSO.*(pi/180));

% ********************** Liquid: 3-PM **********************
theta1_3PM = 23.02;  % Sample 4
theta2_3PM = 41.20;  % Sample 11
Theta_3PM = [theta1_3PM, theta2_3PM];
Cos_th_3PM = cos(Theta_3PM.*(pi/180));

% ***********************************************************
F_PC_new = [f1, f2];
F_diff = 1;
eps = 0.005;
counter = 0;
while (F_diff > eps)
    error = 1;
    ep = 1e-6;
    counter = counter + 1
    F_PC = F_PC_new;
    while (error > ep)
        Cos_th_act_PC = (Cos_th_PC + F_PC - 1)./F_PC;
        cos_th_act_PC = mean(Cos_th_act_PC);
        error = std(Cos_th_act_PC);
        Cos_th_act_PC = ones(1,length(F_PC))*cos_th_act_PC;
        F_PC = (Cos_th_PC - 1)./(Cos_th_act_PC - 1);
    end

    F_DMSO = F_PC;
    error = 1;
    while (error > ep)
        Cos_th_act_DMSO = (Cos_th_DMSO + F_DMSO - 1)./F_DMSO;
        cos_th_act_DMSO = mean(Cos_th_act_DMSO);
        error = std(Cos_th_act_DMSO);
        Cos_th_act_DMSO = ones(1,length(F_DMSO))*cos_th_act_DMSO;
        F_DMSO = (Cos_th_DMSO - 1)./(Cos_th_act_DMSO - 1);
    end

    F_diff = max(abs(F_PC - F_DMSO));
    F_PC_new = F_DMSO;
    plot(counter,F_diff,**r');hold on; pause(0.05)
end
theta_act_PC = acos(cos_th_act_PC)*180/pi;
theta_act_DMSO = acos(cos_th_act_DMSO)*180/pi;

F = (F_PC + F_DMSO)/2;

Example 2: Solve the case of Sample 7 and Sample 8. Both made of NMC532-NMP

f1 = 1;
f2 = 1;

% **** Contact angle with probe liquid: Propylene Carbonate ************
theta1_PC = 18.29; % Sample 7
theta2_PC = 24.25; % Sample 8
Theta_PC = [theta1_PC, theta2_PC];
Cos_th_PC = cos(Theta_PC.*(pi/180));

% **** Contact angle with probe liquid: Dimethyl Sulfoxide *************
theta1_DMSO = 19.35; % Sample 7
theta2_DMSO = 25.80; % Sample 8
Theta_DMSO = [theta1_DMSO, theta2_DMSO];
Cos_th_DMSO = cos(Theta_DMSO.*(pi/180));

% **** Contact angle with probe liquid: 3-PM (Nicotinyl Alcohol) *****
theta1_3PM = 25.53; % Sample 7
theta2_3PM = 33.65; % Sample 8
Theta_3PM = [theta1_3PM, theta2_3PM];
Cos_th_3PM = cos(Theta_3PM.*(pi/180));

F_PC_new = [f1, f2];
F_diff = 1;
eps = 0.005;
counter = 0;
while (F_diff > eps)
    error = 1;
    ep = 1e-6;
    counter = counter + 1
    F_PC = F_PC_new;
    while (error > ep)
        Cos_th_act_PC = (Cos_th_PC + F_PC - 1)./F_PC;
        cos_th_act_PC = mean(Cos_th_act_PC);
        error = std(Cos_th_act_PC);
        Cos_th_act_PC = ones(1,length(F_PC))*cos_th_act_PC;
        F_PC = (Cos_th_PC - 1)./(Cos_th_act_PC - 1);
    end
    F_DMSO = F_PC;
    error = 1;
    while (error > ep)
        Cos_th_act_DMSO = (Cos_th_DMSO + F_DMSO - 1)./F_DMSO;
        cos_th_act_DMSO = mean(Cos_th_act_DMSO);
        error = std(Cos_th_act_DMSO);
\[
\text{Cos}_{\text{th act}}_{\text{DMSO}} = \text{ones}(1, \text{length}(F_{\text{DMSO}}))*\text{cos}_{\text{th act}}_{\text{DMSO}}; \\
F_{\text{DMSO}} = (\text{Cos}_{\text{th DMSO}} - 1)/(\text{Cos}_{\text{th act DMSO}} - 1);
\]

end

\[
F_{3PM} = F_{\text{DMSO}}; \\
\text{error} = 1; \\
\text{while} \ (\text{error} > \text{ep})
\]

\[
\text{Cos}_{\text{th act 3PM}} = (\text{Cos}_{\text{th 3PM}} + F_{3PM} - 1)/F_{3PM}; \\
\text{cos}_{\text{th act 3PM}} = \text{mean}(\text{Cos}_{\text{th act 3PM}}); \\
\text{error} = \text{std}(\text{Cos}_{\text{th act 3PM}}); \\
\text{Cos}_{\text{th 3PM}} = \text{ones}(1, \text{length}(F_{3PM}))*\text{cos}_{\text{th act 3PM}}; \\
F_{3PM} = (\text{Cos}_{\text{th 3PM}} - 1)/(\text{Cos}_{\text{th act 3PM}} - 1);
\]

end

\[
F_{\text{diff}} = \text{max}([\text{max}(\text{abs}(F_{\text{PC}} - F_{\text{DMSO}})), \text{max}(\text{abs}(F_{\text{PC}} - F_{3PM}))]); \\
F_{\text{PC new}} = F_{3PM}; \\
\text{plot}(\text{counter}, F_{\text{diff}}, '*' \text{'r'}); \text{hold on}; \text{pause}(0.05)
\]

end

% Actual Contact Angle of Propylene Carbonate
\[
\text{theta act PC} = \text{acos}(\text{cos}_{\text{th act PC}})*180/\pi;
\]

% Actual Contact Angle of Dimethyl Sulfoxide
\[
\text{theta act DMSO} = \text{acos}(\text{cos}_{\text{th act DMSO}})*180/\pi;
\]

% Actual Contact Angle of Nicotinyl Alcohol
\[
\text{theta act 3PM} = \text{acos}(\text{cos}_{\text{th act 3PM}})*180/\pi;
\]

% Final Surface solid fraction Vector
\[
F = (F_{\text{PC}} + F_{\text{DMSO}} + F_{3PM})/3;
\]

% first element reflects the surface solid fraction of sample 7 and the %second element that of sample 8

% Result:
\[
\text{F} = [0.3552, 0.6189]
\]

% theta act = [30.95, 32.86, 43.35];

Based on two different surface textures, we obtained the following results: \( f \) for Sample 7 is 0.3552, \( f \) for Sample 8 is 0.6189, intrinsic contact angle for PL1 (propylene carbonate) is 30.95°, intrinsic contact angle for PL2 (nicotinyl alcohol) is 43.35°, and intrinsic contact angle for PL3 (dimethyl sulfoxide) is 32.86°.

Example 3: Solve the case of Samples 1, 5, 6, 7 and 8. All made of NMC532-NMP

%Initial Condition for solid fraction of all 5 samples
\[
f1 = 1; \\
f2 = 1; \\
f3 = 1; \\
f4 = 1; \\
f5 = 1;
\]

% **** Contact Angles with Liquid: PC (Propylene Carbonate) ***************
\[
\text{theta1 PC} = 11.19; \ % \text{Sample 1} \\
\text{theta2 PC} = 10.60; \ % \text{Sample 5} \\
\text{theta3 PC} = 19.08; \ % \text{Sample 6} \\
\text{theta4 PC} = 18.29; \ % \text{Sample 7} \\
\text{theta5 PC} = 24.25; \ % \text{Sample 8} \\
\text{Theta PC} = [\text{theta1 PC}, \text{theta2 PC}, \text{theta3 PC}, \text{theta4 PC}, \text{theta5 PC}];
\]

\[
\text{Cos th PC} = \text{cos}(\text{Theta PC}.*(\pi/180));
\]

% **** Contact Angles with Liquid: DMSO (Dimethyl Sulfoxide) ***************
\[
\text{theta1 DMSO} = 14.88; \ % \text{Sample 1}
\]

\]

\[
\text{theta act DMSO} = \text{acos}(\text{cos}_{\text{th act DMSO}})*180/\pi;
\]

\[
\text{theta act 3PM} = \text{acos}(\text{cos}_{\text{th act 3PM}})*180/\pi;
\]

\[
\text{cos}_{\text{th act 3PM}} = \text{mean}(\text{Cos}_{\text{th act 3PM}}); \\
\text{error} = \text{std}(\text{Cos}_{\text{th act 3PM}}); \\
\text{Cos}_{\text{th 3PM}} = \text{ones}(1, \text{length}(F_{3PM}))*\text{cos}_{\text{th act 3PM}};
\]

\[
\text{Cos}_{\text{th act 3PM}} = (\text{Cos th act 3PM} + F_{3PM} - 1)/F_{3PM}; \\
\text{cos}_{\text{th act 3PM}} = \text{mean}(\text{Cos}_{\text{th act 3PM}}); \\
\text{error} = \text{std}(\text{Cos}_{\text{th act 3PM}}); \\
\text{Cos}_{\text{th 3PM}} = \text{ones}(1, \text{length}(F_{3PM}))*\text{cos}_{\text{th act 3PM}};
\]

end

\[
\text{F diff} = \text{max}([\text{max}(\text{abs}(F_{\text{PC}} - F_{\text{DMSO}})), \text{max}(\text{abs}(F_{\text{PC}} - F_{3PM}))]); \\
F_{\text{PC new}} = F_{3PM}; \\
\text{plot}(\text{counter}, F_{\text{diff}}, '*' \text{'r'}); \text{hold on}; \text{pause}(0.05)
\]

end

% Actual Contact Angle of Propylene Carbonate
\[
\text{theta act PC} = \text{acos}(\text{cos}_{\text{th act PC}})*180/\pi;
\]

% Actual Contact Angle of Dimethyl Sulfoxide
\[
\text{theta act DMSO} = \text{acos}(\text{cos}_{\text{th act DMSO}})*180/\pi;
\]

% Actual Contact Angle of Nicotinyl Alcohol
\[
\text{theta act 3PM} = \text{acos}(\text{cos}_{\text{th act 3PM}})*180/\pi;
\]

% Final Surface solid fraction Vector
\[
F = (F_{\text{PC}} + F_{\text{DMSO}} + F_{3PM})/3;
\]

% first element reflects the surface solid fraction of sample 7 and the %second element that of sample 8

% Result:
\[
\text{F} = [0.3552, 0.6189]
\]

% theta act = [30.95, 32.86, 43.35];

Based on two different surface textures, we obtained the following results: \( f \) for Sample 7 is 0.3552, \( f \) for Sample 8 is 0.6189, intrinsic contact angle for PL1 (propylene carbonate) is 30.95°, intrinsic contact angle for PL2 (nicotinyl alcohol) is 43.35°, and intrinsic contact angle for PL3 (dimethyl sulfoxide) is 32.86°.

Example 3: Solve the case of Samples 1, 5, 6, 7 and 8. All made of NMC532-NMP

%Initial Condition for solid fraction of all 5 samples
\[
f1 = 1; \\
f2 = 1; \\
f3 = 1; \\
f4 = 1; \\
f5 = 1;
\]

% **** Contact Angles with Liquid: PC (Propylene Carbonate) ***************
\[
\text{theta1 PC} = 11.19; \ % \text{Sample 1} \\
\text{theta2 PC} = 10.60; \ % \text{Sample 5} \\
\text{theta3 PC} = 19.08; \ % \text{Sample 6} \\
\text{theta4 PC} = 18.29; \ % \text{Sample 7} \\
\text{theta5 PC} = 24.25; \ % \text{Sample 8} \\
\text{Theta PC} = [\text{theta1 PC}, \text{theta2 PC}, \text{theta3 PC}, \text{theta4 PC}, \text{theta5 PC}];
\]

\[
\text{Cos th PC} = \text{cos}(\text{Theta PC}.*(\pi/180));
\]

% **** Contact Angles with Liquid: DMSO (Dimethyl Sulfoxide) ***************
\[
\text{theta1 DMSO} = 14.88; \ % \text{Sample 1}
\]

\]
\begin{verbatim}
theta2_DMSO = 13.92;  \% Sample 5
theta3_DMSO = 21.57;  \% Sample 6
theta4_DMSO = 19.35;  \% Sample 7
theta5_DMSO = 25.80;  \% Sample 8
Theta_DMSO = [theta1_DMSO, theta2_DMSO, theta3_DMSO, theta4_DMSO, theta5_DMSO];
Cos_th_DMSO = cos(Theta_DMSO.*(pi/180));

% **** Contact Angles with Liquid: 3-PM (Nicotinyl Alcohol) **************
theta1_3PM = 19.64;  \% Sample 1
theta2_3PM = 18.92;  \% Sample 5
theta3_3PM = 26.65;  \% Sample 6
theta4_3PM = 25.53;  \% Sample 7
theta5_3PM = 33.65;  \% Sample 8
Theta_3PM = [theta1_3PM, theta2_3PM, theta3_3PM, theta4_3PM, theta5_3PM];
Cos_th_3PM = cos(Theta_3PM.*(pi/180));

F_PC_new = [f1, f2, f3, f4, f5];
F_diff = 1;
eps = 0.15;
counter = 0;
while (F_diff > eps)
    error = 1;
    ep = 1e-6;
    counter = counter + 1
    F_PC = F_PC_new;
    while (error > ep)
        Cos_th_act_PC = (Cos_th_PC + F_PC - 1)./F_PC;
        cos_th_act_PC = mean(Cos_th_act_PC);
        error = std(Cos_th_act_PC);
        Cos_th_act_PC = ones(1,length(F_PC))*cos_th_act_PC;
        F_PC = (Cos_th_PC - 1)./(Cos_th_act_PC - 1);
    end

    F_DMSO = F_PC;
    error = 1;
    while (error > ep)
        Cos_th_act_DMSO = (Cos_th_DMSO + F_DMSO - 1)./F_DMSO;
        cos_th_act_DMSO = mean(Cos_th_act_DMSO);
        error = std(Cos_th_act_DMSO);
        Cos_th_act_DMSO = ones(1,length(F_DMSO))*cos_th_act_DMSO;
        F_DMSO = (Cos_th_DMSO - 1)./(Cos_th_act_DMSO - 1);
    end

    F_3PM = F_DMSO;
    error = 1;
    while (error > ep)
        Cos_th_act_3PM = (Cos_th_3PM + F_3PM - 1)./F_3PM;
        cos_th_act_3PM = mean(Cos_th_act_3PM);
        error = std(Cos_th_act_3PM);
        Cos_th_act_3PM = ones(1,length(F_3PM))*cos_th_act_3PM;
        F_3PM = (Cos_th_3PM - 1)./(Cos_th_act_3PM - 1);
    end

    F_diff = max([max(abs(F_PC - F_DMSO)),max(abs(F_PC - F_3PM))]);
    F_PC_new = F_3PM;
    plot(counter,F_diff,'r');hold on; pause(0.05)
end
\end{verbatim}
% Actual Contact Angle of Propylene Carbonate
theta_act_PC = acos(cos_th_act_PC)*180/pi;
% Actual Contact Angle of Dimethyl Sulfoxide
theta_act_DMSO = acos(cos_th_act_DMSO)*180/pi;
% Actual Contact Angle of Nicotinyl Alcohol
theta_act_3PM = acos(cos_th_act_3PM)*180/pi;
% Final Surface solid fraction Vector
F = (F_PC + F_DMSO + F_3PM)./3;
% with five elements each representing the surface solid fraction of samples 1, 5, 6, 7, and 8, respectively

% Result:
% F = [0.1833, 0.1652, 0.4068, 0.3587, 0.6251]
% theta_act = [28.66, 34.07, 44.92]

Based on five different surface textures, we obtained the following results: f for Sample 7 is 0.3587, f for Sample 8 is 0.6251, intrinsic contact angle for PL1 (propylene carbonate) is 28.66°, intrinsic contact angle for PL2 (nicotinyl alcohol) is 44.92°, and intrinsic contact angle for PL3 (dimethyl sulfoxide) is 34.07°. These values are very close to those obtained based on two surface textures.

**Calculation of Bulk Porosity of Each Electrode Sample**

The bulk porosity of the electrode samples was calculated based on the measured thickness of the electrodes following the procedure provided by Haselrieder et al. [41]. The formula is shown below.

\[
\text{Porosity} = \left( \frac{\text{Volume of Voids}}{\text{Total Volume}} \right) \times 100\%
\]
\[
= \left( \frac{\text{Total Volume} - \text{Volume of the Solid}}{\text{Total Volume}} \right) \times 100\%
\]
\[
= (1 - \frac{\text{Volume of the Solid}}{\text{Total Volume}}) \times 100\%
\]
\[
= \left[ 1 - \frac{\text{Mass Loading of the Coating Layer}}{\text{Average Density of the Powder Mixture}} \right] \times 100\%
\]
\[
= \left[ 1 - \frac{\text{Mass Loading of the Coating Layer}}{\text{Average Density of the Powder Mixture} \times \text{Coating Layer Thickness}} \right] \times 100\%
\]

The Average Density of the Powder Mixture is calculated based on the individual mass concentration of each electrode component and the density of each component.