Supporting Information

A Rough Electrode Creates Excess Capacitance in Thin Film Capacitors

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Determining $C_m$ with impedance spectroscopy

The most conventional method to find the electrical capacitance of a capacitor is impedance spectroscopy. In this method, a low amplitude AC signal is applied to the capacitor and the output current in the circuit is measured. From the resulting voltage-current relation which can be simplified to a form similar to Ohm’s relation, the impedance response of the capacitor is measured:

$$I(\omega) = \frac{V(\omega)}{Z(\omega)} \quad (S1)$$

where $\omega$ and $Z(\omega)$ are the angular frequency and impedance, respectively. The measurements can be performed by commercially available impedance meters. The response of a capacitor to the variations of the voltage is given as:

$$I(\omega) = \omega j C V(\omega) \quad (S2)$$

where, $j = (-1)^{1/2}$. Therefore, capacitance can be calculated from the real part of the following equation:

$$C(\omega) = \frac{1}{j \omega Z(\omega)} = -\frac{Z'}{\omega|Z|^2} - j \frac{Z''}{\omega|Z|^2} \quad (S3)$$

where $Z'$ is the real and $Z''$ is the imaginary part of the impedance response of the capacitor. In this work, we perform impedance spectroscopy with an AC signal of 10 mV from 1 MHz to 100 Hz. We set the DC bias well below the built-in voltage of the capacitors to make the contacts non-injecting and deplete capacitors from space charges. Then we model the measured impedance with a suitable equivalent circuit. Normally a series and a parallel resistance companies the capacitor representing the series resistance of the contacts/interfaces and the leakage paths in the sample, respectively. Therefore,
the impedance response of a non-ideal simple capacitor follows equation S4 and can be modeled by the equivalent circuit shown in Figure S2.

\[ Z = R_s + \frac{R_p}{1 + j\omega R_p C} \]  

(S4)

Figure S2. The equivalent circuit used to model the impedance response of a simple capacitor with one rough and one smooth electrode.

From Figure S3, it is clear that the assigned equivalent circuit model fits the impedance response of PDEG-1 with smooth and rough electrodes (the topography of the smooth and rough electrodes are shown in Figure 4a,b). This means that, it is difficult to disentangle the capacitance of the rough interface from the overall capacitance through equivalent circuit model.

Figure S3. Left: The admittance \((Y \equiv Z')\) of the rough and smooth capacitors measured via impedance spectroscopy and fitted by the equivalent circuit model of Figure S2. Right: The capacitance calculated from the equation S3 (real part) divided by the capacitance calculated from equation 1 for the rough and smooth capacitors. The fitting is performed by the equivalent circuit model of Figure S2. The series resistance of contacts outweighs the capacitance at high frequencies. By subtracting \(R_s\) from the real part of the impedance, frequency independent values for \(C_m/C_0\) are obtained (empty symbols) at high frequencies just as low frequencies.
Determining $C_0$

The accuracy of $C_0$ depends on the accuracy of the area of the capacitors ($A$), and the average thickness of the filler ($h_0$).

To approve a linear dependence of $C_0$ on the area of the electrodes, we pattern four capacitors with different areas for a specific thickness of the filler as shown on Figure S4.

This design also allows us to access the surface of the filler for AFM imaging. The images obtained from the bare surface of the filler gives us information about the topology of the interface at the top electrode because almost the same pattern is expected at the interface.

The thickness of thin films is normally measured by profilometers. The resolution of the profilometers, however, is not adequate for resolving the nanometer scaled features of the rough surfaces. As shown on Figure S5, the scanning tip of profilometers normally has larger size than the nanoscale features of the surface, therefore cannot follow the height fluctuations of the surface precisely. As a consequence, an overestimated value for the thickness of the rough films is obtained with profilometry as illustrated schematically in Figure S5.

To find the average height of a rough surface precisely, it is better to scan a trench on the film by tapping mode AFM. We obtain the topographic information of the film with higher lateral and height resolution compared with profilometers which allows us to find $h_0$ precisely. Figure S6 shows a step height fit performed by Gwyddion software of a trench created in the film.
Another method to find the average thickness of a rough film correctly, is to make a trench in the film together with the top metallic electrode. Via finding the step height of the trench by profilometer and subtracting the thickness of the top electrode, the average thickness of the film is obtained. The studied films in this work showed film thickness obtained by this method equal to the step height of the bare films acquired by tapping mode AFM.

Figure S6. Screenshot of an edge height fit performed by Gwyddion software. The step profile shown on the image is scanned by tapping mode AFM with the scanning area of 14 μm by 14 μm.
Determining the roughness parameters

We use a theoretical approach to find the capacitive contribution of the roughness at the interface of thin film capacitors. This approach, attributes the capacitive effect of the interface to the effective area of the electrode increased by roughness, and the enhanced electric field at the nanoscale hills and valleys of the electrode. To be able to use this model, we need to describe the roughness with roughness parameters. For this purpose we find the HHCF (equation 3) by Gwyddion, a free software for visualization and analysis of scanning probe microscopy data. However, for some surfaces the topology is not adequately correlated within the scan size of the AFM (see Figure S7). In other words, we cannot find the correlation length correctly using equation 3a,b due to large topological features. Despite a clear influence of the roughness on the capacitance of PTeEG-1, for instance, we could find the roughness originated capacitance terms only for the samples processed from CHCl₃. The rest of the samples did not have adequately correlated topology to find roughness parameters (see Table S1). As a rule of thumb, the scan size should be at least 10 times bigger that the largest features, so that we can correctly find the roughness parameters of the entire surface.

Figure S7. AFM image of PTETRA-1 processed from solvent mixture of CHCl₃:ODCB (1:1) as an example of uncorrelated topology within the scanned area.

By plugging the obtained roughness parameters into equation 5, we find the interface roughness contribution in the total capacitance that we determine via impedance spectroscopy. In this way we are able to eliminate this contribution from the total capacitance and find the electrical capacitance intrinsic to the filler material.

Table S1, lists the roughness parameters calculated from the height difference correlation function and the roughness factors of the top electrode’s interface. For fullerene derivatives \( a_c \) is set to 1 nm, approximately equal to the size of buckyballs. For PVDF-TrFE capacitors, \( a_c \) is set to 70 nm to obtain \( C_{eff} \approx 1 \).
Table S1. Film specifications and roughness parameters of PDEG-1, PTeEG-2, PTeEG-1 and PVDF-TrFE, and the corresponding values of \( C_w/C_0 \) before and after eliminating the excess capacitance of the rough electrode. The values shown in red are obtained from the samples that exceed the weak roughness limit (\( \sigma/\xi < 0.05\% \)) set for the calculations.

| Solvent          | \( h_0 \) (nm) | \( C_w/C_0 \) | \( \alpha \) | \( \sigma \) (nm) | \( \xi \) (nm) | \( \sigma/\xi \) (%) | \( \sigma/h_0 \) (%) | \( f_{r1} \) | \( f_{r2} \) | \( C_{ef} \) = \( C_{f}/C_0 \) |
|------------------|----------------|---------------|-------------|------------------|--------------|-----------------|-------------------|------------|-----------|----------------|
| **PVDF-TrFE (\( \alpha_c = 70 \text{ nm} \))** |
| cyclohexane      | 662.7±4.6      | 10.9±0.1      | 0.95        | 6.2              | 1265.1       | 0.49            | 0.9               | 0.00       | 0.00      | 1.00           | 10.9 |
| cyclohexane      | 248.5±1.9      | 10.9±0.1      | 0.73        | 8.3              | 394.3        | 2.11            | 3.4               | 0.01       | 0.01      | 1.01           | 10.8 |
| cyclohexane      | 269.8±1.8      | 10.9±0.4      | 0.79        | 7.8              | 401.0        | 1.94            | 2.9               | 0.01       | 0.01      | 1.01           | 10.8 |
| cyclohexane      | 191.8±1.5      | 11.0±0.2      | 0.76        | 11.1             | 337.9        | 3.29            | 5.8               | 0.01       | 0.01      | 1.02           | 10.8 |
| cyclohexane      | 226.4±1.5      | 11.3±0.1      | 0.82        | 19.8             | 414.6        | 4.78            | 8.7               | 0.03       | 0.01      | 1.04           | 10.9 |
| **PTeEG-2 (\( \alpha_c = 1 \text{ nm} \))** |
| CHCl \(_3\)      | 169.9±1.7      | 5.5±0.1       | 0.85        | 3.9              | 144.9        | 2.70            | 2                 | 0.04       | 0.00      | 1.04           | 5.3  |
| CHCl \(_3\)      | 105.4±1.5      | 5.6±0.1       | 0.81        | 2.4              | 100.4        | 2.45            | 2                 | 0.03       | 0.00      | 1.04           | 5.4  |
| CHCl \(_3\)      | 158.1±1.5      | 5.6±0.1       | 0.89        | 6.7              | 221.7        | 3.06            | 4                 | 0.04       | 0.00      | 1.05           | 5.4  |
| CHCl \(_3\)      | 164.9±1.3      | 5.9±0.1       | 0.88        | 6.6              | 216.7        | 3.08            | 4                 | 0.05       | 0.00      | 1.05           | 5.6  |
| CHCl \(_3\)      | 173.9±1.1      | 5.9±0.1       | 0.80        | 3.6              | 106.1        | 3.36            | 2                 | 0.07       | 0.00      | 1.08           | 5.5  |
| \( C_6H_{14}Cl: CHCl \(_3\) (1:1)\) | 87.0±2.4      | 6.2±0.2       | 0.87        | 19.8             | 515.9        | 3.83            | 23                | 0.1        | 0.06      | 1.16           | 5.3  |
| \( C_6H_{14}Cl: CHCl \(_3\) (1:7)\) | 114.7±1.7      | 6.3±0.1       | 0.84        | 27.5             | 680.4        | 4.05            | 24                | 0.16       | 0.07      | 1.23           | 5.1  |
| \( C_6H_{14}Cl: CHCl \(_3\) (1:17)\) | 122.4±2.0      | 6.8±0.1       | 0.85        | 28.9             | 634.8        | 4.42            | 23                | 0.17       | 0.06      | 1.24           | 5.5  |
| \( C_6H_{14}Cl: CHCl \(_3\) (1:2)\) | 159.3±2.1      | 7.4±0.1       | 0.90        | 36.1             | 633.8        | 5.70            | 23                | 0.19       | 0.06      | 1.25           | 5.9  |
| \( C_6H_{14}Cl: CHCl \(_3\) (1:12)\) | 170.0±5.5      | 7.7±0.3       | 0.90        | 35.0             | 641.8        | 5.46            | 21                | 0.17       | 0.05      | 1.23           | 6.3  |
| **PTeEG-1 (\( \alpha_c = 1 \text{ nm} \))** |
| CHCl \(_3\)      | 138.9±1.8      | 5.1±0.1       | 0.82        | 13.8             | 475.2        | 2.91            | 10                | 0.09       | 0.01      | 1.1            | 4.6  |
| CHCl \(_3\)      | 138.2±1.6      | 5.2±0.1       | 0.79        | 13.0             | 455.4        | 2.86            | 9                 | 0.11       | 0.01      | 1.12           | 4.6  |
| CHCl \(_3\)      | 133.8±1.8      | 5.2±0.1       | 0.81        | 13.2             | 468.2        | 2.81            | 10                | 0.09       | 0.01      | 1.10           | 4.7  |
| CHCl \(_3\)      | 151.8±2.8      | 5.3±0.1       | 0.80        | 16.7             | 492.5        | 3.40            | 11                | 0.15       | 0.02      | 1.16           | 4.6  |
| CHCl \(_3\)/ODCB (1:1) | 226.3±3.0 | 6.0±0.1 | | | | | | | | | |
| CHCl \(_3\)/ODCB (1:1) | 200.7±1.9 | 6.6±0.1 | | | | | | | | | |
| CHCl \(_3\)/ODCB (1:1) | 163.5±3.3 | 5.7±0.1 | | | | | | | | | |
| CHCl \(_3\)/ODCB (1:1) | 59.8±1.9 | 5.6±0.1 | | | | | | | | | |
| CHCl \(_3\)/ODCB (1:1) | 62.2±1.8 | 6.6±0.1 | | | | | | | | | |

- **Cyclohexane**
- **Solvent**
- **CHCl \(_3\)**
- **ODCB**
- **PTeEG**
- **PVDF-TrFE**
- **Values**
- **Roughness Parameters**
- **Specifications**
- **$h_0$** (nm)
- **$C_w/C_0$**
- **$\alpha$**
- **$\sigma$ (nm)**
- **$\xi$ (nm)**
- **$\sigma/\xi$ (%)**
- **$\sigma/h_0$ (%)**
- **$f_{r1}$**
- **$f_{r2}$**
- **$C_{ef} = C_{f}/C_0$**

Note: The table includes data for various solvents and conditions, with specific parameters such as $h_0$, $C_w/C_0$, $\alpha$, $\sigma$, $\xi$, $\sigma/\xi$, $\sigma/h_0$, $f_{r1}$, $f_{r2}$, and $C_{ef} = C_{f}/C_0$. The values are presented in different solvent systems, including cyclohexane, CHCl \(_3\), and ODCB. The table also includes roughness parameters and calculations for PDEG-1, PTeEG-2, PTeEG-1, and PVDF-TrFE.