

Electronic Supplementary Information - ESI

Clay Nanomaterial Thin Film Electrodes for Electrochemical Energy

Storage Applications

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ESI 1. Supplementary experimental details.

Materials

Laponite RD, a synthetic smectic clay with a density of 2.65 g cm^{-3} was obtained from Southern Clay Products and used as received without any further purification. 3-Trihydroxysilylpropyl-methylphosphonate organosilane was purchased from Santa Cruz Biotechnology (Germany). Deionized water was used to prepare aqueous solutions ($\geq 18 \text{ M}\Omega$).

Preparation of Laponite and organosilane intercalated Laponite solutions

Two solutions were prepared. The first one contains 2% of well-dispersed clay suspension that is prepared by adding 1 g of Laponite nanoparticles into 50 mL of water at a pH of 9.6. The dispersion was stirred at room temperature overnight. The second solution was prepared by adding 0.2 g of 3-Trihydroxysilylpropyl-methylphosphonate organosilane to the first solution under stirring. The mixture was stirred for 24 h at room temperature to yield Laponite-organosilane nanocomposite.

Laponite/Phosphonate films elaboration

Large particles were removed from the solution by filtration (1.2 μm filter) before coating. The films were deposited by dip-coating in a glove box onto cleaned substrates with a withdrawal speed of 60 mm/min. and silicon wafer were used as substrate depending on electrochemical experiment and SEM study. The coating layer is then dried at 70°C for 10 min. High quality transparent films are obtained and studied at room temperature. The film thickness was in the range from 370 to 400 nm, determined from SEM cross section.

Characterization

Morphology: The morphology of the nanostructures was characterized with a high-resolution scanning electron microscope (SEM), equipped with a scanning transmission electron microscopy (STEM) detector and an energy dispersive spectroscopy (EDS) detector (Ultra

Plus, Zeiss, Oberkochen, Germany). Atomic force microscope (AFM, Nanowizard, JPK Instruments, Berlin) images were obtained in tapping mode using super-sharp silicon tips (Nanosensors, Neuchatel, Switzerland).

Structure : X-ray diffraction (X'Pert Pro system, PANalytical, Almelo, The Netherlands) patterns were obtained in grazing incident geometry with fixed angle of 1.5° and 2Θ step of 0.05° using monochromatic Cu $K\alpha$ radiation ($(\lambda=1.5418\text{\AA})$). The d-spacings were calculated from the angular 2Θ positions of the 001 reflection peaks.

A Bruker Raman microscope was used to acquire Raman scattering spectra over a range of $70-3600\text{ cm}^{-1}$, with a spectral resolution of $3-5\text{ cm}^{-1}$, using a backscattering configuration with a $20\times$ objective excited with a 532 nm laser diode. Data were collected on numerous spots on the sample and recorded with a fully focused laser power of 20 mW. Each spectrum was accumulated four times with an integration time of 10 s. The Raman signal was recorded using a CCD camera. Silicon substrate Raman peak position (520 cm^{-1}) was used to calibrate spectral frequency.

Electrochemical characterization: The electrochemical experiments were performed at room temperature in a standard three-electrode cell. The cyclic voltammograms (CVs) were obtained using an electrochemical workstation (ZAHNER IM6e, Kronach, Germany), and charging-discharging tests were performed using a Source Meter (Keithley 2400, Cleveland, OH, USA). A Pt mesh and hydroflex (H_2 reference electrode) were used as counter and reference electrodes, respectively. All potentials are referred to the standard hydrogen electrode (SHE).

To measure the capacitance of the electrodes, CVs were recorded in an aqueous electrolyte containing 1 M KCl between 0 and 1 V at different scan rates. The charge-discharge behavior at different current densities and long-term cycling stability were tested in the same electrolyte at a potential window 0-600 mV. Before each electrochemical experiment,

nitrogen was bubbled in the electrolyte for 30 min. The electrochemical experiments were conducted on a minimum of three to five samples each. The specific capacitances were calculated from the CVs using Equation 1¹³ :

$$\frac{C}{m} = \frac{I}{2VS} \quad (1),$$

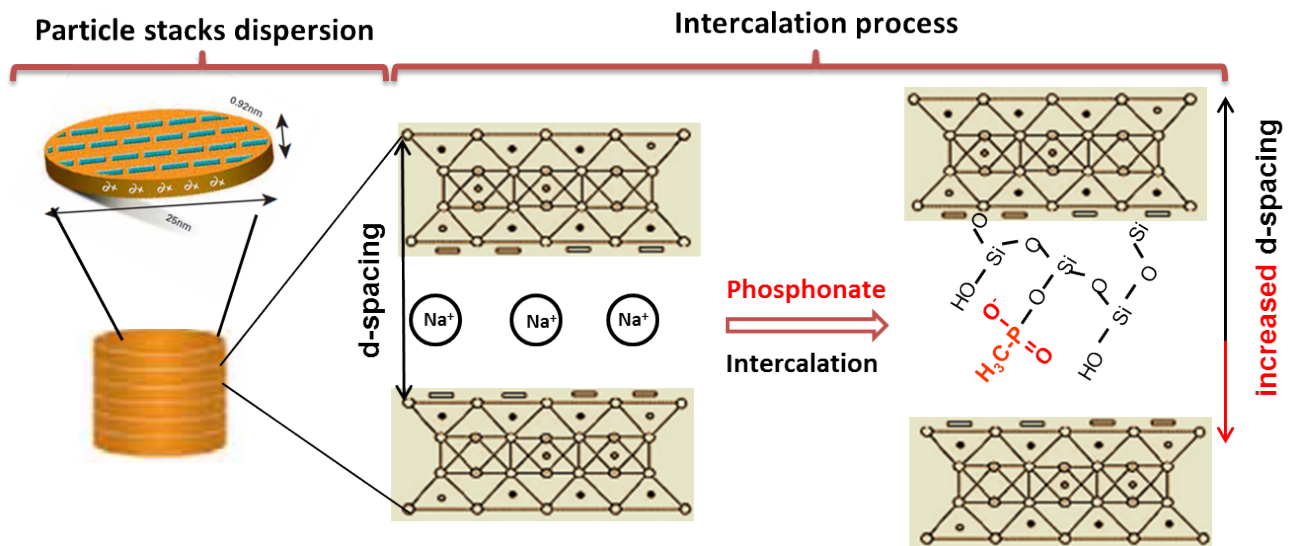
where C/m is the specific capacitance (F/g), I the integrated area (VA) of the CV curve in one complete cycle, V the potential window (V), S the scan rate (V/s), and m the mass (g) of the film estimated from the mass of non-volatile spaces present in the solution.

Charging-discharging experiments were conducted at constant current density. From the slope of the charge–discharge curve, the specific capacitance is deduced using Equation 2:

$$\frac{C}{m} = \frac{I\Delta t}{\Delta V} \quad (2),$$

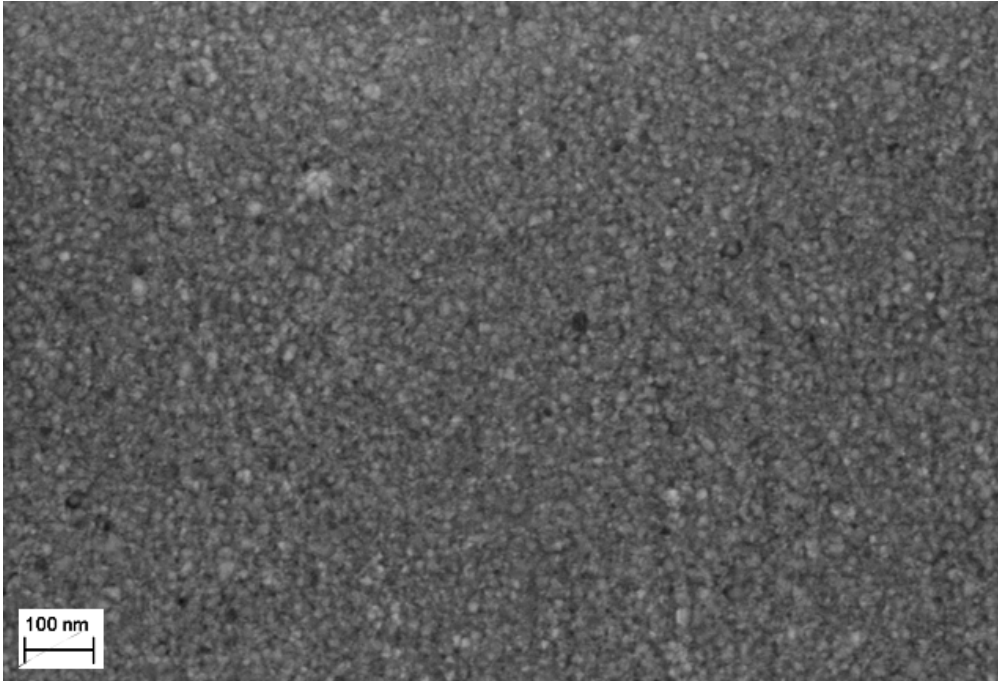
where I is the applied current (A), Δt the discharge time (s) and ΔV the potential window.

ESI2: Schemes of Laponite particles, the layered smectite structure and an intercalated organosilane, in this case Trihydroxysilylpropyl-methylphosphonate.

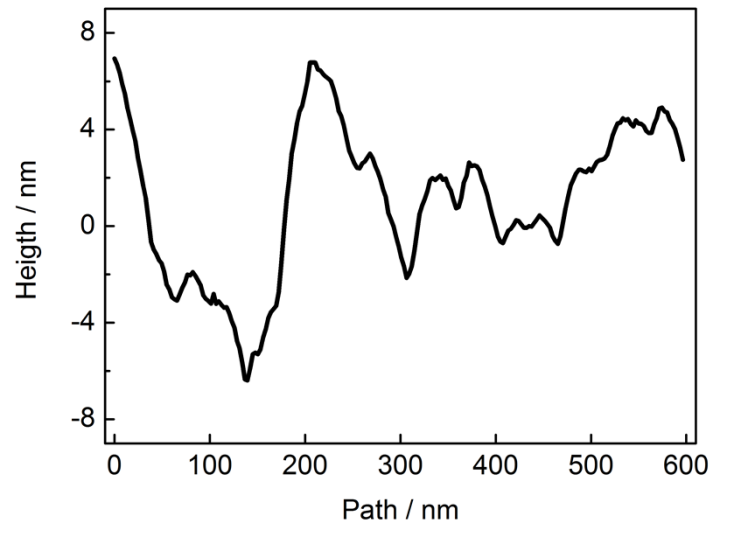
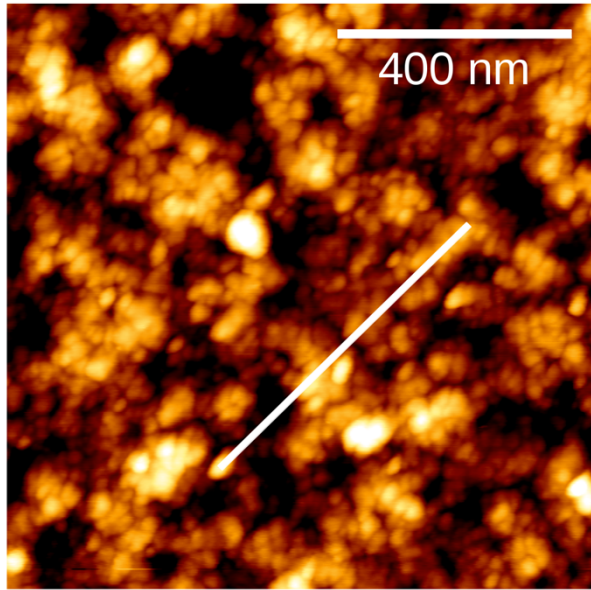


XRD patterns show a slight shift in the basal plane diffraction peak to higher d-spacing in the nanocomposite sample, although this shift is difficult to assess due to the large value of the FWHM of the 001 peak. Using the Bragg's equation, the corresponding increase in the spacing between the (001) planes of the clay layers. We think that the reactive alkoxyethyl head group of the silane molecule also adsorbs on the clay and can form a covalent bond with the edge silanols as reported by Herrera et al. [J. Mater. Chem., 2005, 15, 863–871]. These species progressively intercalate within the clay platelets giving rise to a gradual increase of the interlayer d₀₀₁ spacing. The intercalation reaction starts at the edges of the laponite microcrystals and the molecules progressively penetrates towards the interior.

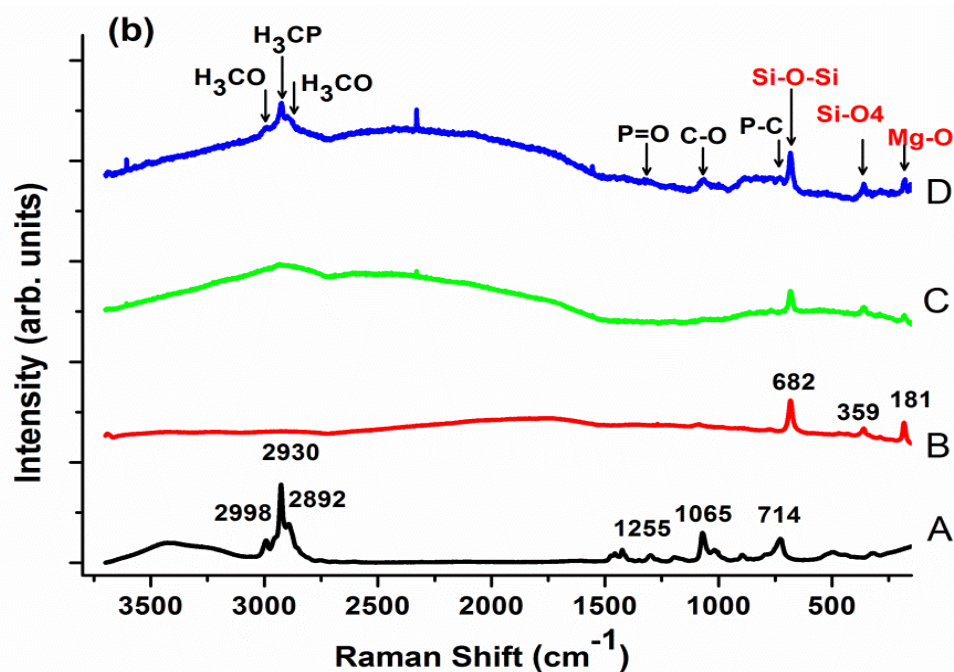
ESI 3. SEM micrograph of the nanocomposite film showing a finer structure than the plain Laponite film



ESI 4. AFM amplitude micrograph and height profile (left) across the white line on micrograph.

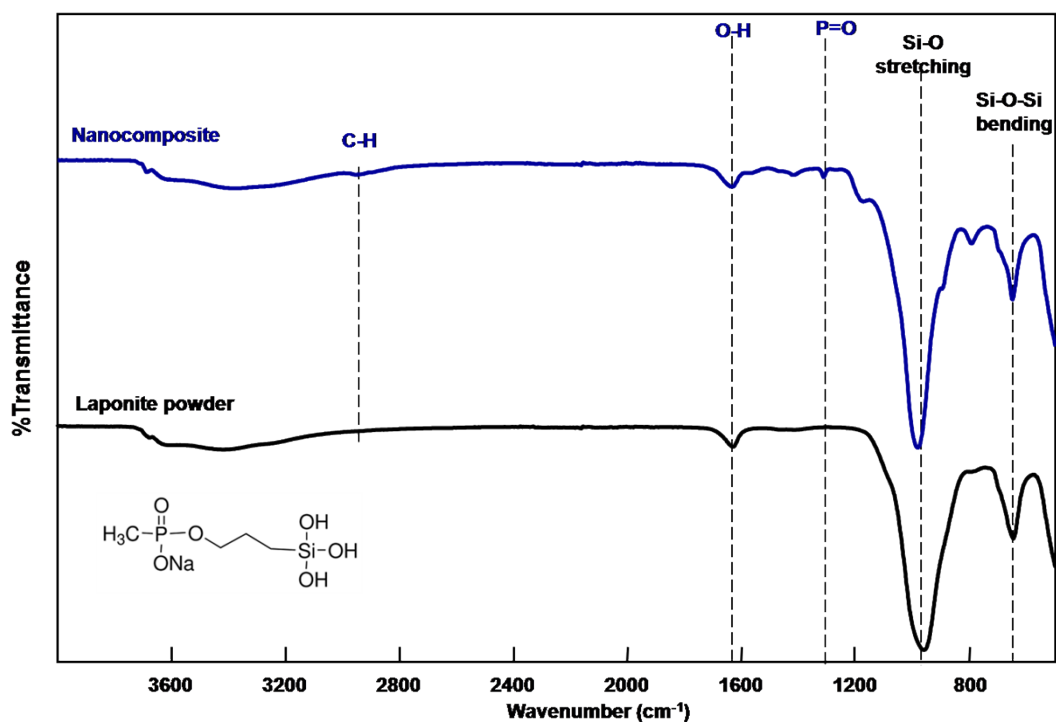


ESI5. Raman scattering spectra of Trihydroxysilylpropyl-methylphosphonate (organosilane) obtained on a drop of the substance (A). The spectra B, C, and D are for powder and films as above. Notice that the spectrum of the nanocomposite film contains characteristic peaks of both Laponite and organosilane.

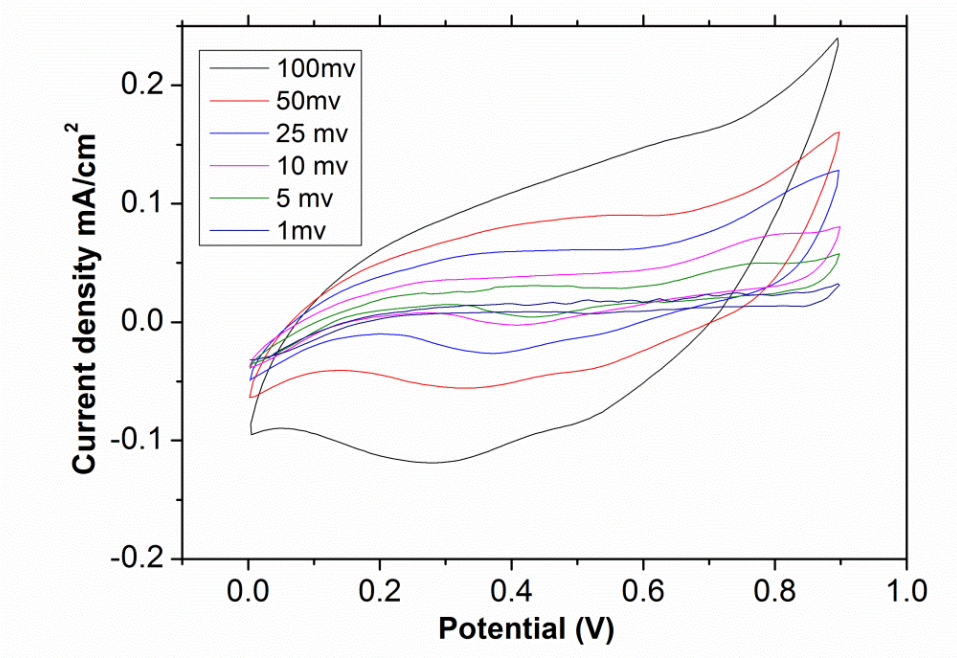


The Raman spectrum of Laponite exhibits a broad shoulder at 3700-3400 cm^{-1} that is usually assigned to surface hydroxyl groups and adsorbed water. In the low energy region, the spectrum shows one band at 682 cm^{-1} assigned to Si-O-Si vibration, one band at 359 cm^{-1} assigned to Si-O bending and one band at 181 cm^{-1} assigned to Mg-O vibration.¹² The nanocomposite shows in principle the same vibrations of the Laponite film in addition to vibrations of the organosilane. Characteristic peaks of the phosphonate organosilane (obtained by measuring a drop of the pure organosilane) appear in the range between 2900 cm^{-1} and 3000 cm^{-1} ; they are attributed to C-H stretching vibration. A sharp peak at 1251 cm^{-1} is ascribed to P=O stretching vibration while the peaks located at 1065 cm^{-1} and 714 cm^{-1} are attributed to the C-O bending and P-C vibration.

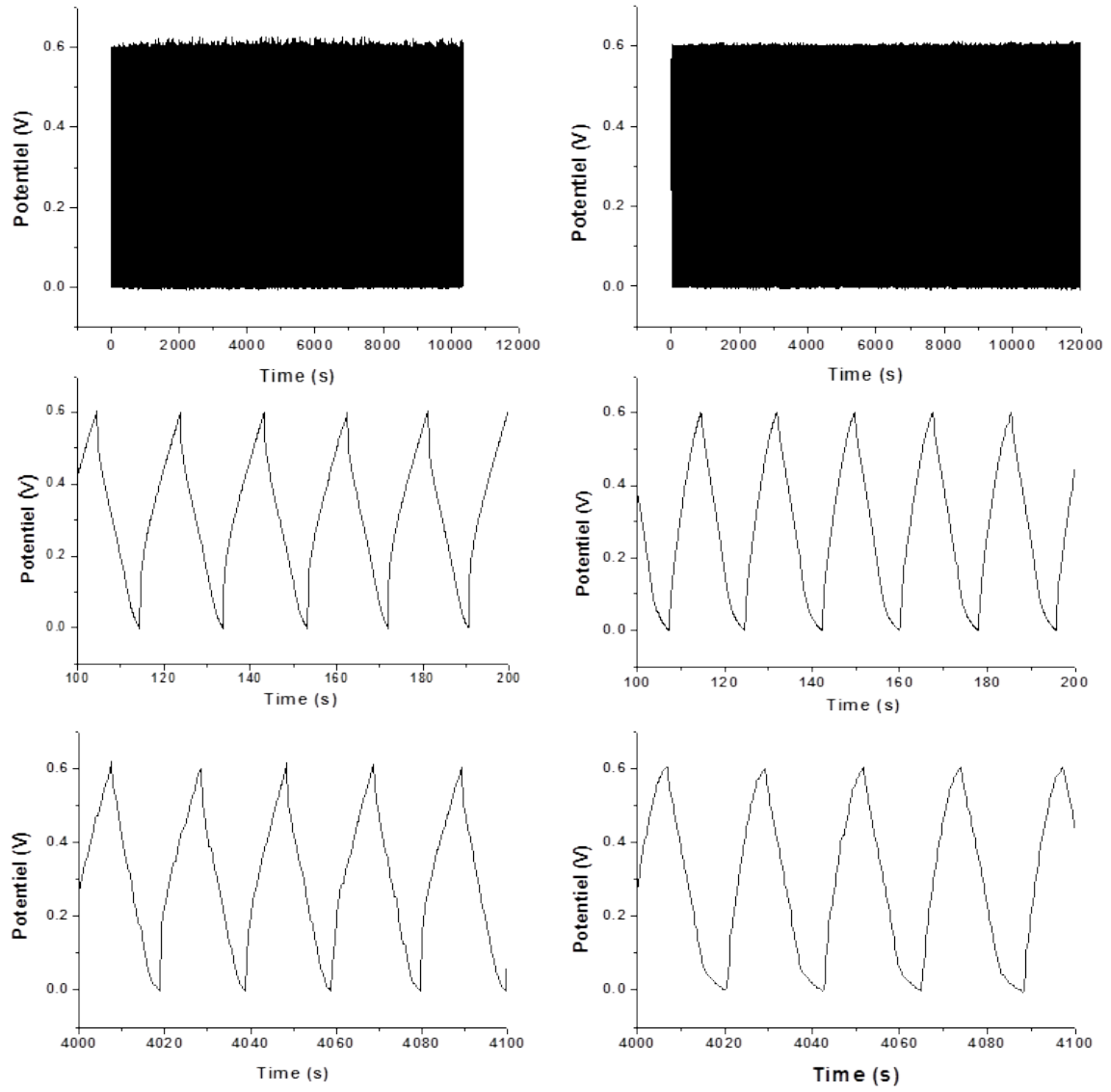
ESI 6. FT-IR spectrum of Laponite and nanocomposite film. The peaks detected at about 1015 cm^{-1} and 470 cm^{-1} are attributed to Si-O band and Si-O bending vibrations, and the peak found at 660 cm^{-1} is for Mg-O.



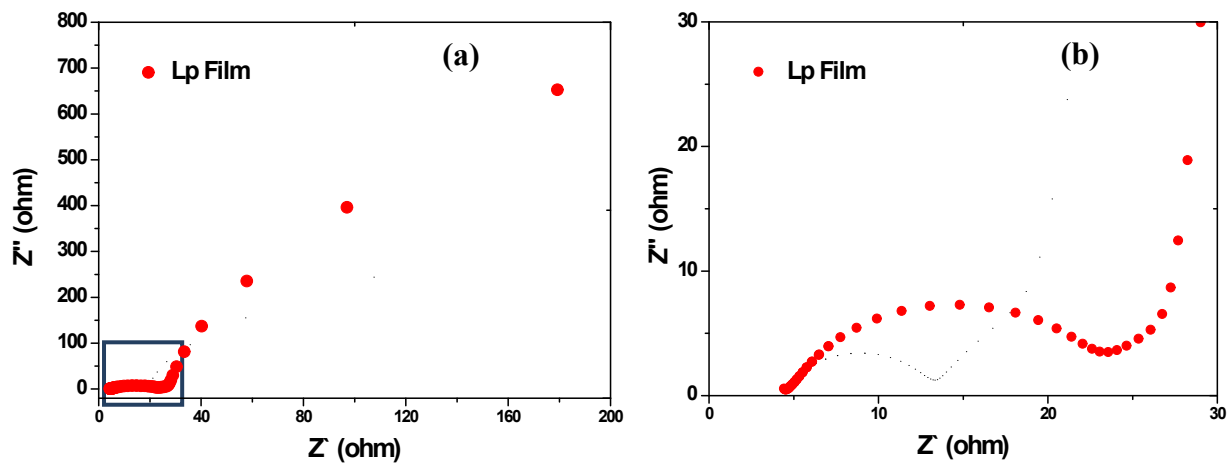
ESI7. The CV curves of the plain Laponite film at different scan rates



ESI8. Long-term cycling test (500 cycles) at a current density of 5 A/g for the Laponite, left and nanocomposite film, right.

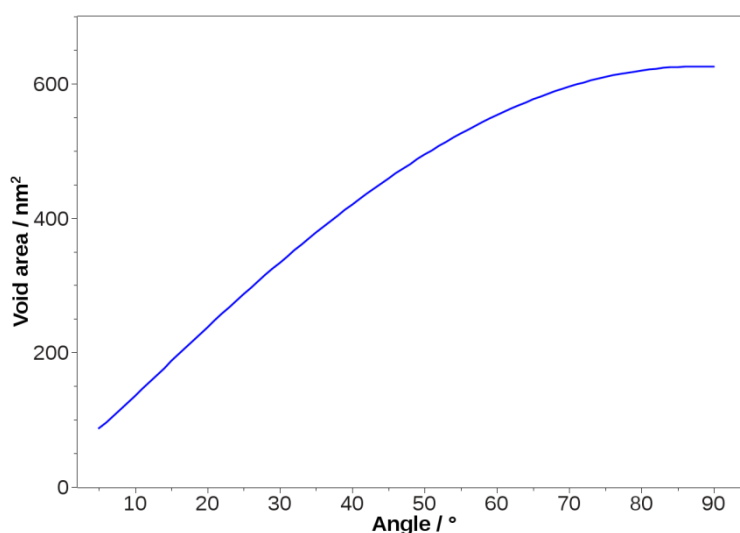
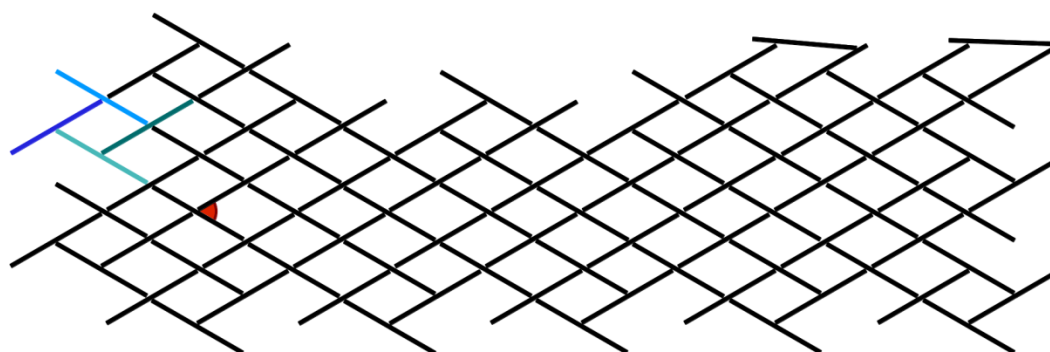


ESI9. (a) Nyquist plots of the electrochemical impedance spectroscopy for Lp Film tested in 1 M KCl, (b) the magnified part of the semicircles.



The capacitive behaviour for the Laponite film (Lp-film) is confirmed via electrochemical impedance spectroscopy (EIS). The ideal Nyquist impedance plot contain a half semicircle at high frequency and a straight line at low frequency, the high frequency part is related to solution resistance (R_s) and the width of the semicircle corresponds to the real impedance such as ionic charge-transfer resistance of composite layer on electrode. [19] From the diameters of the semicircle, the charge-transfer resistance of Laponite film was calculated to be 15Ω .

ESI10. Schematic drawing of a stretched card-house structure (upper Figure)



On the left the building block from four Laponite disks is emphasized. The volume of the parallelograms is governed by the sine of the angle shown in red. The ideal structure will be disturbed as indicated for the surface on the right side. The drawing describes a smooth transition from the rectangular card house into the brick structure by decreasing one angle from 90° to 0°. Since the volume decrease of the rhomboids is governed only by the sine of this angle, large voids stay present inside for a large part of such a transition (lower diagram). No extended regular structures are expected for the films, but this idea illustrates the possibility that locally large voids can be maintained during film building.

