**SAXS Signature of the Lamellar Ordering of Ionic Domains of Perfluorinated Sulfonic-Acid Ionomers by Electric and Magnetic Field-Assisted Casting.**

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**Abstract**: This supplementary material contains time-resolved small angle X-ray scattering (SAXS) data for Nafion samples to test the morphological stability under the X-ray beam, SAXS measurements for Nafion as a function of equivalent weight in the cesium form to confirm the lamellar shape of the ionic domains. Duplicate and triplicate SAXS measurements were performed to ensure the reproducibility of nanostructured membranes by electric and magnetic field-assisted casting. In addition AFM phase images of the membranes structured by electric and magnetic fields; and the associated AFM topography height profile matching the length scales obtained by SAXS, the dimensional variations of the ElecCast and MagCast with increasing temperature are presented. Duplicate of the fuel cell performance for MagCast and finally, the pictures of the nanostructured ElecCast and MagCast, revealing their differentiated optical properties are shown.

**Keywords**: Block Copolymers; Ionomers; Magnetic Alignment; Electric Alignment; Lamellar; Swelling; Anisotropic Conductivity; Perfluorosulfonate Sulfonic-Acid Ionomers.

*Time-resolved SAXS measurements to ensure no X-ray beam degradation of Nafion.*

To ensure that there is no damage of the samples in the SAXS experiments, time-resolved SAXS measurements in 50 frames of 200s, totalizing (10000s / 166 min) and the measurements are shown in **Fig. S1**.

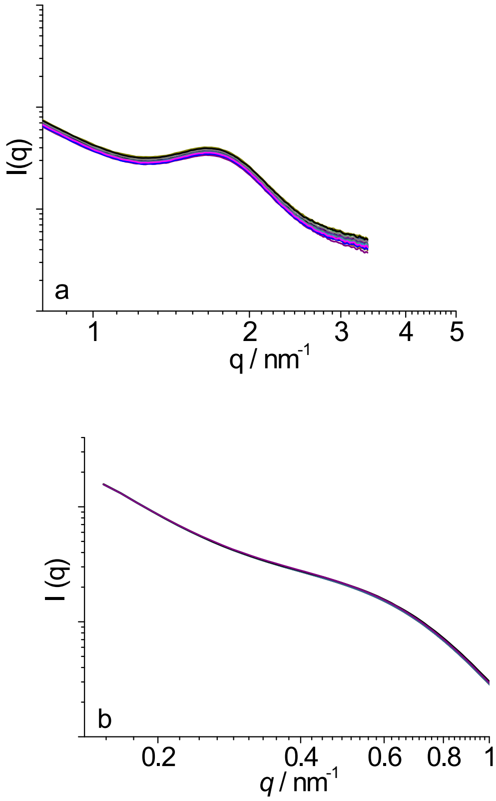



**Figure S1.** Time-resolved SAXS measurements of Nafion in 50 frames of 200s: (a) ionomer and (b) matrix peaks.

As can be seen in **Fig. S1**, the fifty SAXS curves performed over a period of 166 min overlap and no detectable changes in the matrix and ionomer peaks are observed, indicating that X-ray beam damage is minimum over this timeframe. The SAXS measurements contained in the manuscript were performed with 10s X-ray beam exposure in which the morphological changes observed are mainly a result of the electric and magnetic field alignment.

*Small angle X-ray scattering (SAXS) of hydrated Nafion-Cs+ with increasing EW*

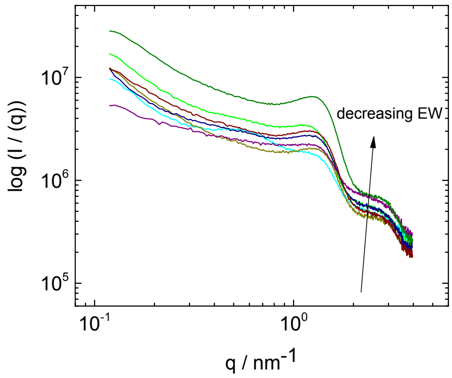



**Figure S2.** SAXS plots of hydrated Nafion-$Cs^+$ with increasing EW.

In **Fig. S2**, the SAXS plots of hydrated Nafion-$Cs^+$ with decreasing *EW* from 1901 to 928 $gEq^{-1}$ are shown. The ionomer peak shows two reflections obeying $q^*$ and $2q^*$, which is indicative of a lamellar arrangement of the ionic phase.

*Duplicates and triplicates of the SAXS measurements obtained for Nafion membranes aligned by electric and magnetic fields.*

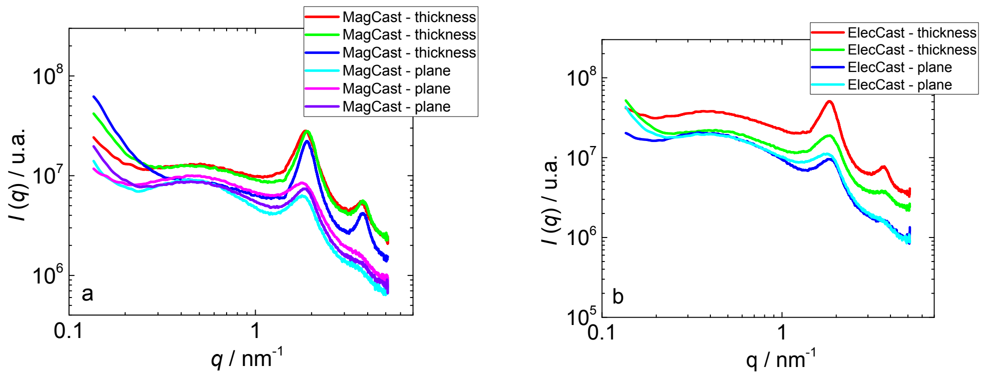



**Figure S3.** SAXS plots of dry Nafion-$H^+$ prepared by magnetic (a) and electric (b) field assisted casting.

The duplicate and triplicate SAXS measurements performed for ElecCast and MagCast, respectively are reproducible, in both thickness and plane directions, as shown in **Fig. S3**, thereby confirming the production of highly ordered ionic domains in Nafion by electric and magnetic field assisted casting.

*Kratky plot of Nafion SAXS curve.*

**Fig. S4** shows the Kratky plot of the SAXS curve of annealed Nafion (**Fig. 2d**), revealing the peaks at $q^*$ (~ 0.22 nm$^{-1}$) and $2q^*$ (~ 0.42 nm$^{-1}$), confirming lamellar reflections in the annealed samples.

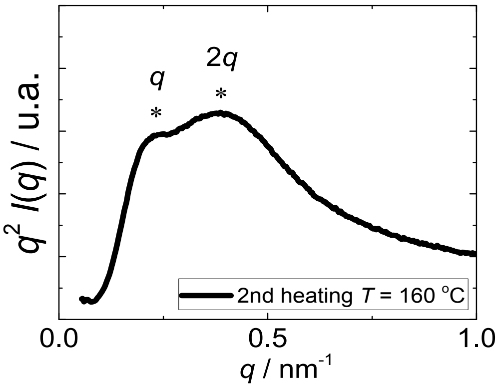



**Figure S4**. Kratky plot of **Fig. 2d** SAXS plot at 160 °C.

*Atomic force microscopy (AFM) phase images of the topography measurements shown in the manuscript.*

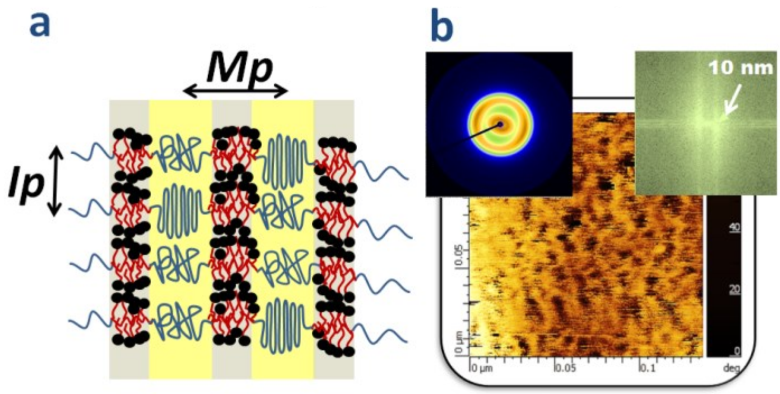



**Figure S5.** (a) Schematic representation of the lamellar stacking of ionic and nonionic domains, indicating the matrix ($M_p$) and ionomer ($I_p$); and (b) AFM phase image of commercial extruded Nafion (N115) film surface in the 150 x 150 nm$^2$ window. The insets show the N115 weak anisotropic 2D pattern alongside the Fourier Transform of the topography.

As Nafion is a statistical copolymer, a higher degree of disordering within the lamella exists as shown in the phase image of extruded Nafion in **Fig. S5b**. The 2D SAXS plots of commercial Nafion, shown in **Fig. S5b** inset, display a weak anisotropic pattern in the films surface due to the extrusion. The matrix peak (**Fig. 2**) and the Fourier Transform (**Fig. S5b**) of such topography match with a periodicity of 10 – 12 nm of bright domains vertically elongated. The darker region corresponds to ionic domains that can be discerned by the strong interactions of these domains with the AFM tip due to Coulombic attraction. In this way, the brighter regions are associated with the TFE separated domains, which are lined up with ionic domains, with a periodicity of ~ 10 nm which is in good agreement with the assignment of the matrix peak in the SAXS plot of Nafion made in **Fig. 2**. In the phase image of N115 (**Fig. S5b**), it is not possible to differentiate shape of the nonionic domains to determine whether it is lamellar or cylindrical. However, based on the SAXS patterns of **Fig. 2** and the AFM image of **Fig. S5b**, the proposed idealized arrangement of ionic and nonionic domains of Nafion is schematized in **Fig. S5a**.

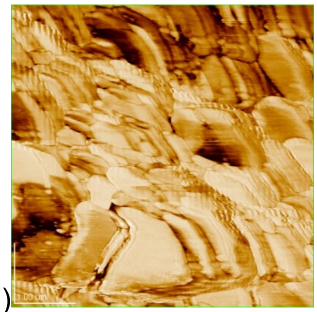
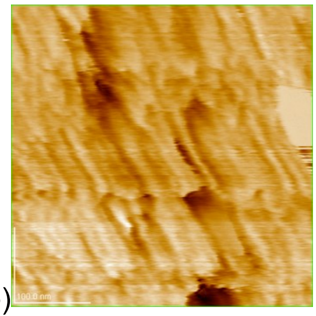
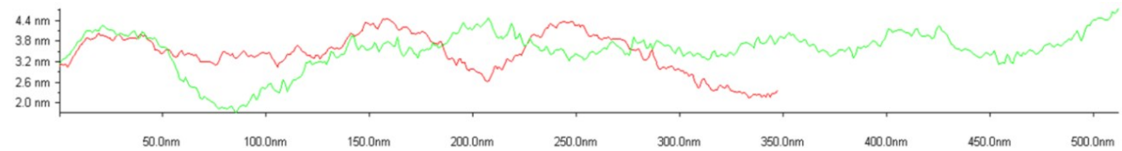
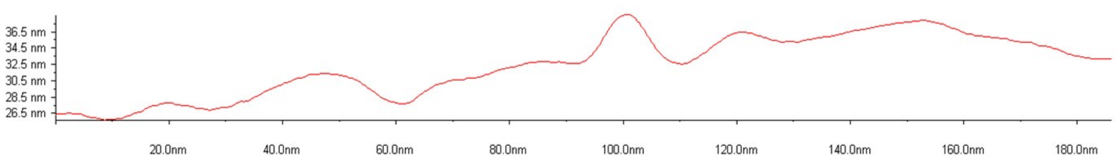
(a)

(b)


**Figure S6.** AFM images of the MagCast (a) and ElecCast (b) samples topography images shown in the manuscript.

**Figs. S6a** and **S6b** show the AFM phase images of **Figs. 6f** and **6h** of the manuscript, respectively. The phase images indicate that the topography contrast observed in **Figs. 6f** and **6h** is a result of distinct phases of nanometer size existing in the sample. **Fig. S6a** shows lamella terraces in MagCast and **Fig. S6b** shows that the lamellar phase in ElecCast is due to the piling up of cylindrical aggregates of ~ 12 nm in diameter and ~ 130 nm in length.

*AFM topography height profile for the corresponding images of Fig. 6.*

(a)


(b)


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c)

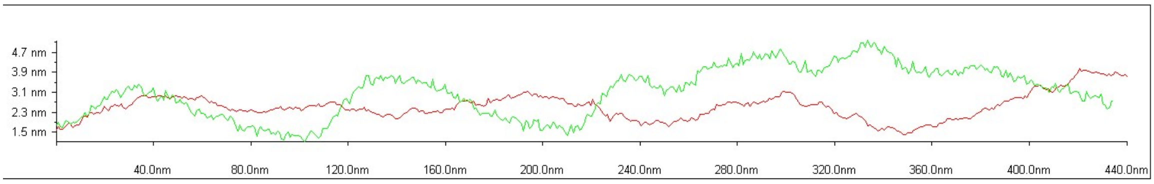


**Figure S7**. AFM topography height profile evidencing the thickness of the stacked lamella for Cast (a), ElecCast (b) and MagCast (c).

AFM measurements were performed to confirm the correlation length and the structural anisotropy observed by SAXS measurements for the samples prepared by electric and magnetic field-assisted casting. The SAXS plots of ElecCast and MagCast support the existence of lamellar morphology with a characteristic dimension of ~ 3 nm. In the AFM measurements, lamellar features vertically stacked were observed in which the height of the topography terraces (**Figs. S7b** and **S7c**) is in the range of 3 – 10 nm, which is in very good agreement with the SAXS data. Therefore, the lamellar thickness and orientation observed by both techniques match confirming the morphological alignment of the film.

*Thickness dependence on temperature for Cast, ElecCast and MagCast*

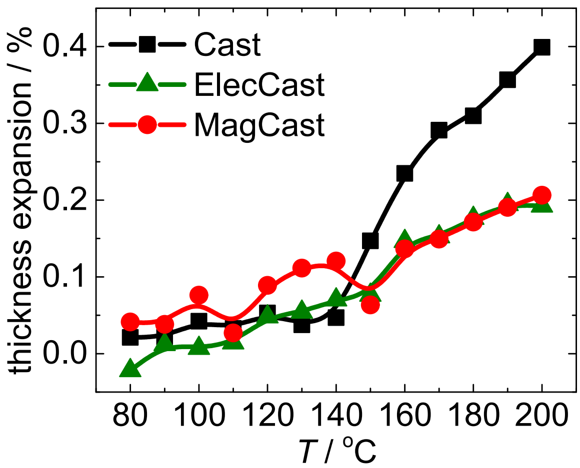


**Figure S8.** Thickness dependence on temperature for Cast, ElecCast and MagCast.

In **Fig. S8**, a higher degree of expansion is found in the thickness direction for the pristine Cast samples, compared to the low thickness dependence on temperature for ElecCast and MagCast.

*Duplicates $H_2/O_2$ polarization curves obtained for Nafion membranes aligned by magnetic field.*

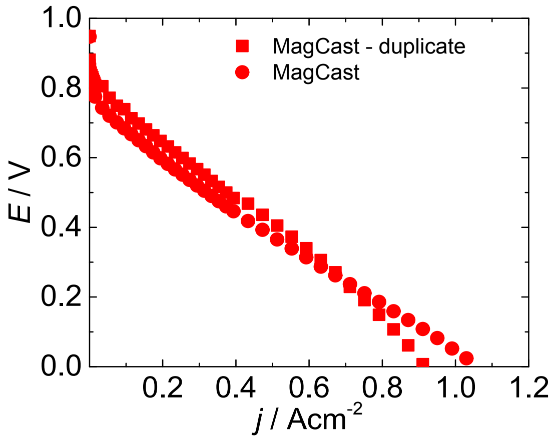


**Figure S9.** $H_2/O_2$ polarization curve for MagCast in duplicate at 80 °C and RH = 100%

In the proof-of-concept fuel cell experiments shown in **Fig. S9**, the MagCast fuel cell performance was obtained in duplicate confirming that the fuel cell performance shown in the manuscript is reproducible.

*Pictures of the ElecCast and MagCast films*

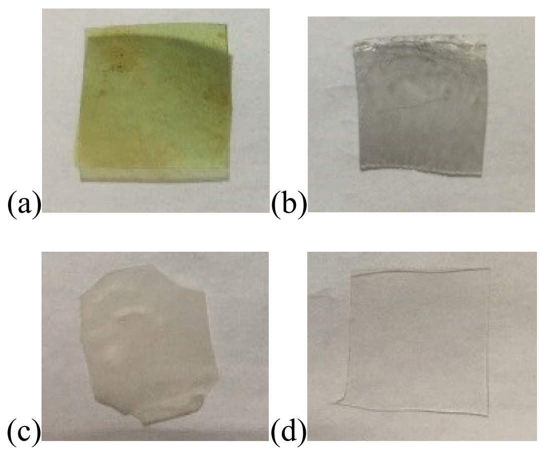


**Figure S10.** ElecCast (a), MagCast (b), Cast (c) and extruded Nafion 115 (d).

**Figure S10** shows that the nanostructured ElecCast (greenish) and MagCast (grayish) membranes displays distinct coloring with respect to the transparent pristine Cast and extruded N115.