



BULGARIAN ACADEMY OF SCIENCES | ENERGY RESOURCES AND ENERGY EFFICIENCY

EIA

Bulgaria

2014

Permittivity Impedance Spectroscopy of porous wet functional ceramics

E. Mladenova*, Z. Stoynov, D. Vladikova, B. Burdin



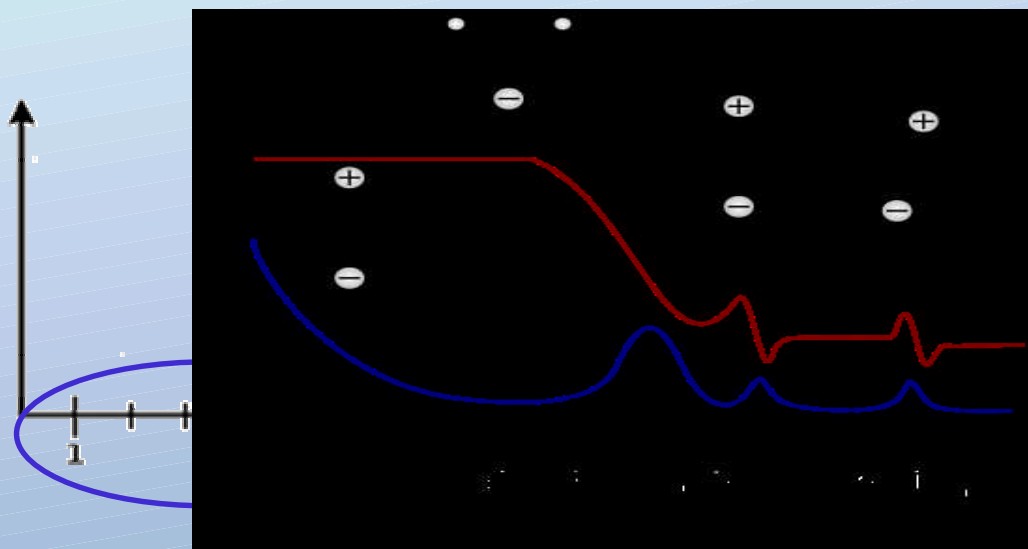
INSTITUTE OF ELECTROCHEMISTRY AND
ACADEMICIAN EVGENI BUDEVSKI ENERGY SYSTEMS



Why Permittivity Spectroscopy

Because:

- Studied of dipoles re-orientation in the AC field
- Large frequency range



PIS

Low frequency range

- Up – expected phenomenon



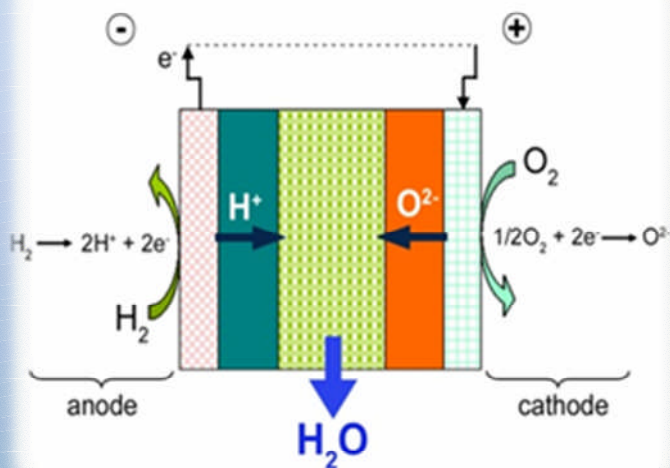
Why porous functional ceramics

Because:

- Functional ceramics are solid non-polarizable dielectrics
- Used for SOFC
- Used for the central membrane of dmFC

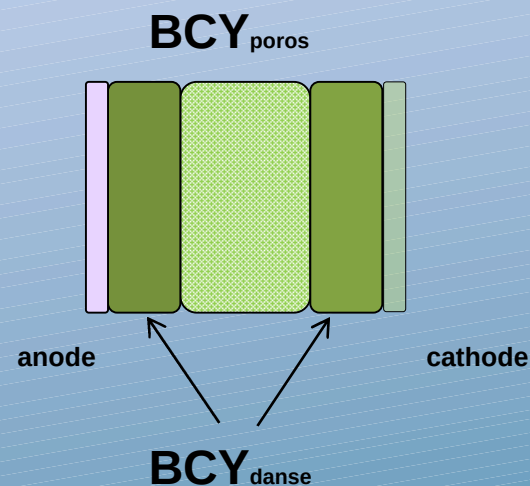
What is dmFC?

BCY/YDC poros



Monolithic type

and





Aim

Investigation of water behaviour in the functional ceramics used as central membrane of the dmFC

Investigation of the frequency dependence of the effective capacitance on:

- Quantity of water in the membrane;
 - Type of porosity (pore-former);
 - Influence on the material of functional ceramics
- composite and monolithic.



$$Z(j\omega) = -j(\omega C)^{-1} \quad (1)$$

$$C = \varepsilon_0 \varepsilon_r S/d \quad (2)$$

$$\varepsilon = \varepsilon' - j\varepsilon'' \quad (3)$$

$$C = C' - jC'' \quad (4)$$

$$Y(j\omega) = 1/Z(j\omega) \quad (5)$$

$$Y(j\omega) = j\omega C = j\omega(C' - jC'') = \omega C'' + j\omega C' \quad (6)$$



Device:

Solartron 1260 FRA

AC signal: 0.1 V– 3 V

Frequency range :

1 MHz – 1 Hz

Type of ceramics:

BCY/YDC, BCY

YDC: $\text{Ce}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ - O^{2-} -type

BCY: $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{2.925}$ - H^{+} -type

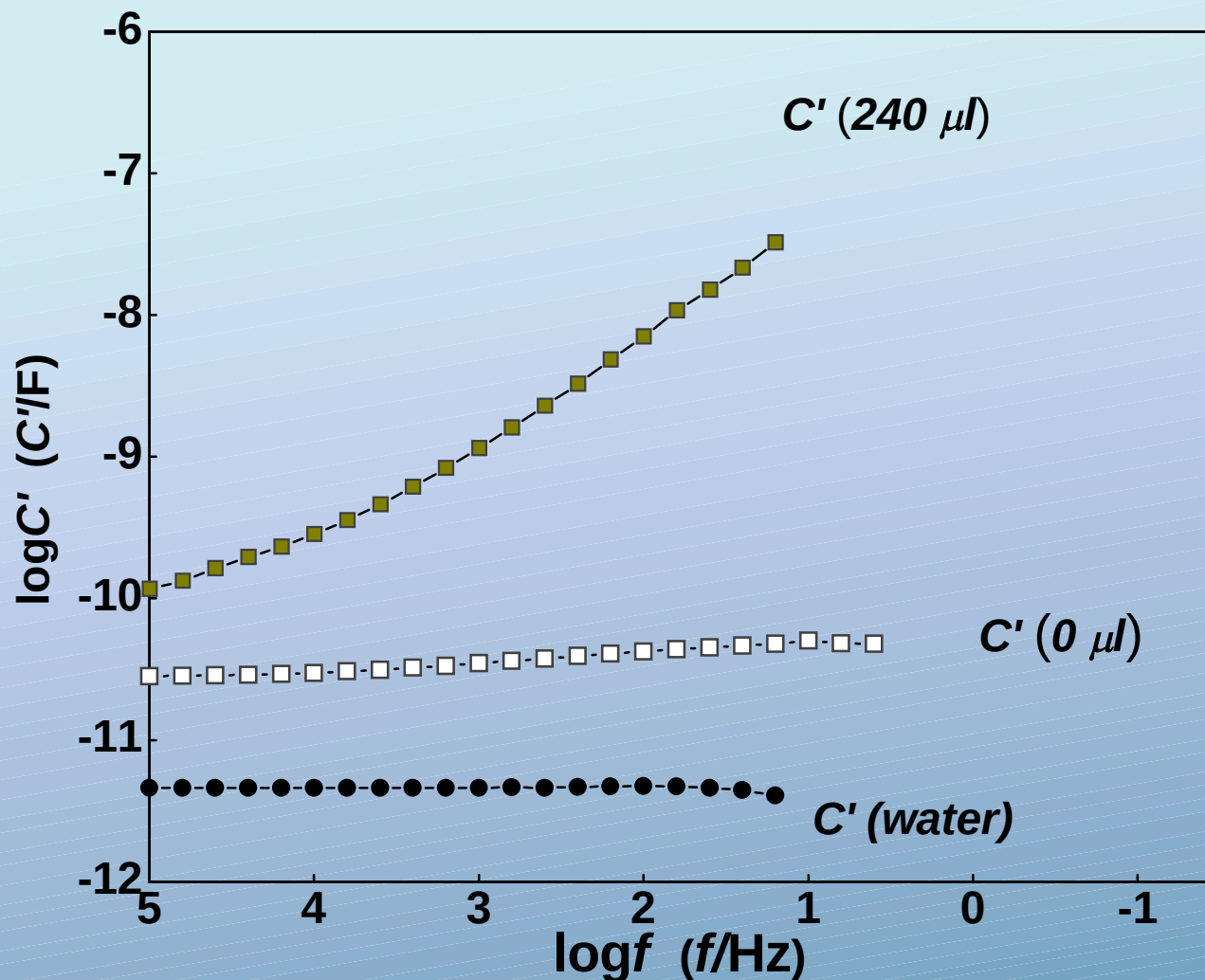
Type of pore former:

starch, graphite

Size: $D = 22.1 \text{ mm}$, $d = 1 \text{ mm}$

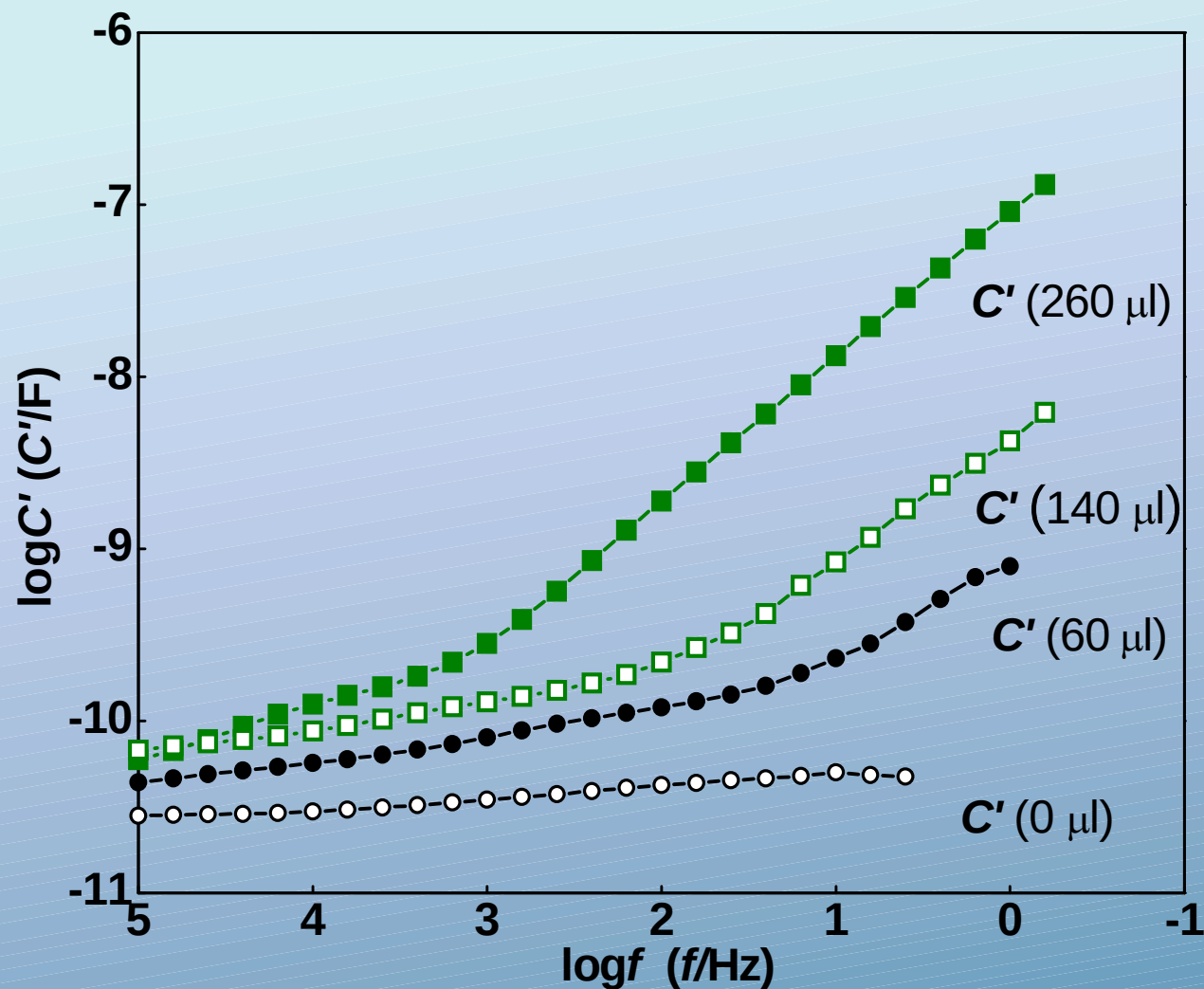


Water behavior on *functional ceramics*





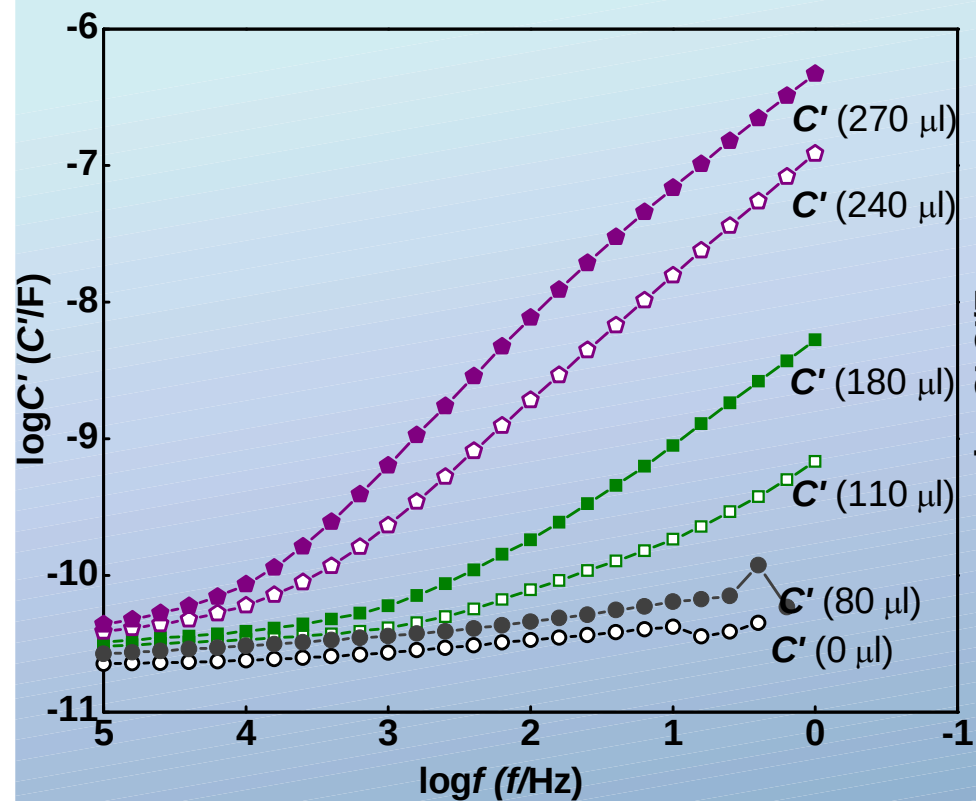
Influence of quantity of water on the effective capacitance



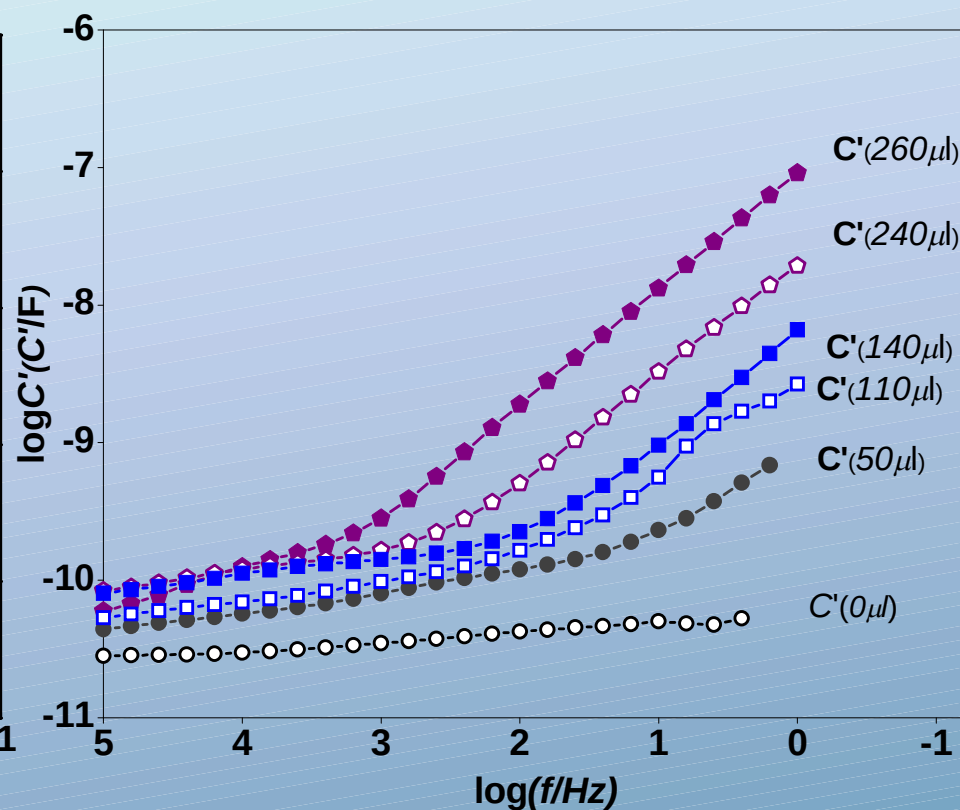


Influence of porosity type (pore former)

2wt% graphite



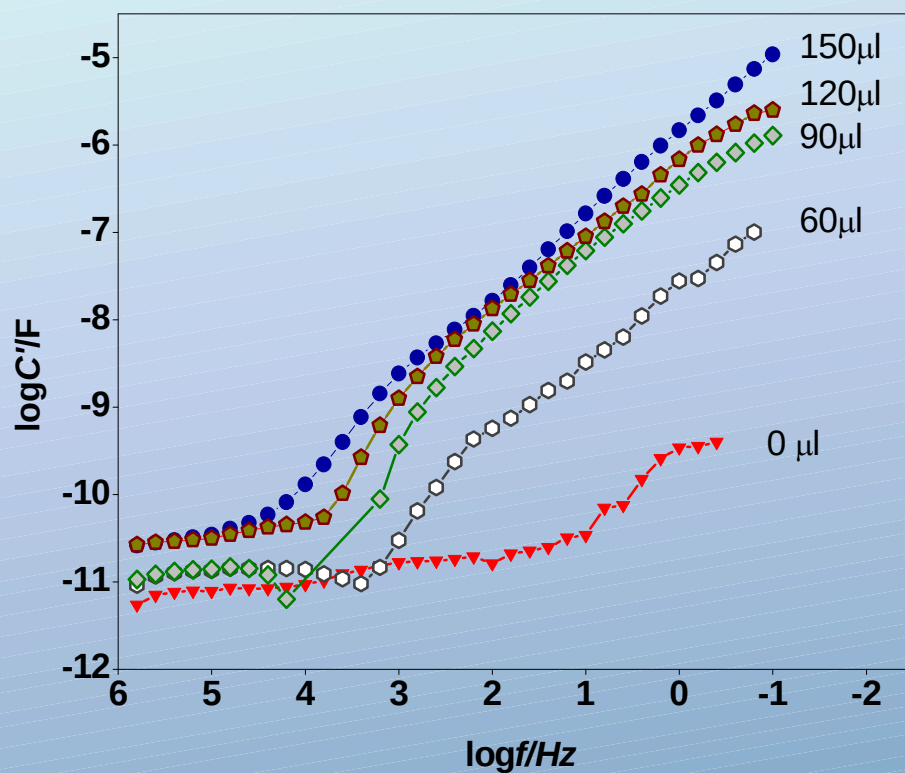
2wt% starch



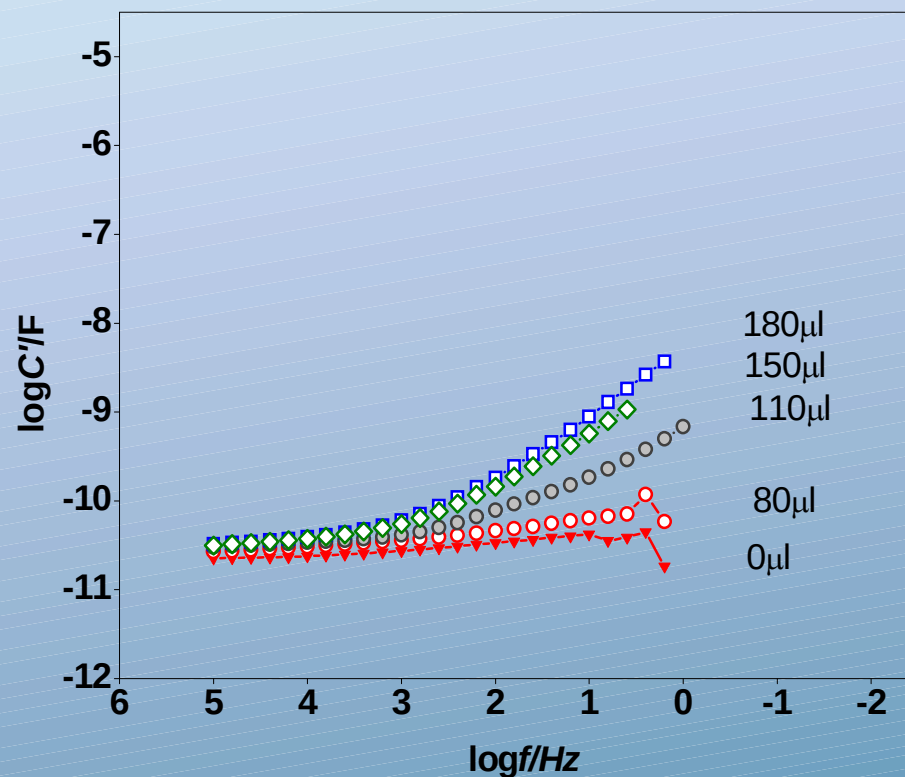


Influence of the Central Membrane material on the frequency dependence

Monolithic BCY15, graphite



BCY15/YDC15, graphite





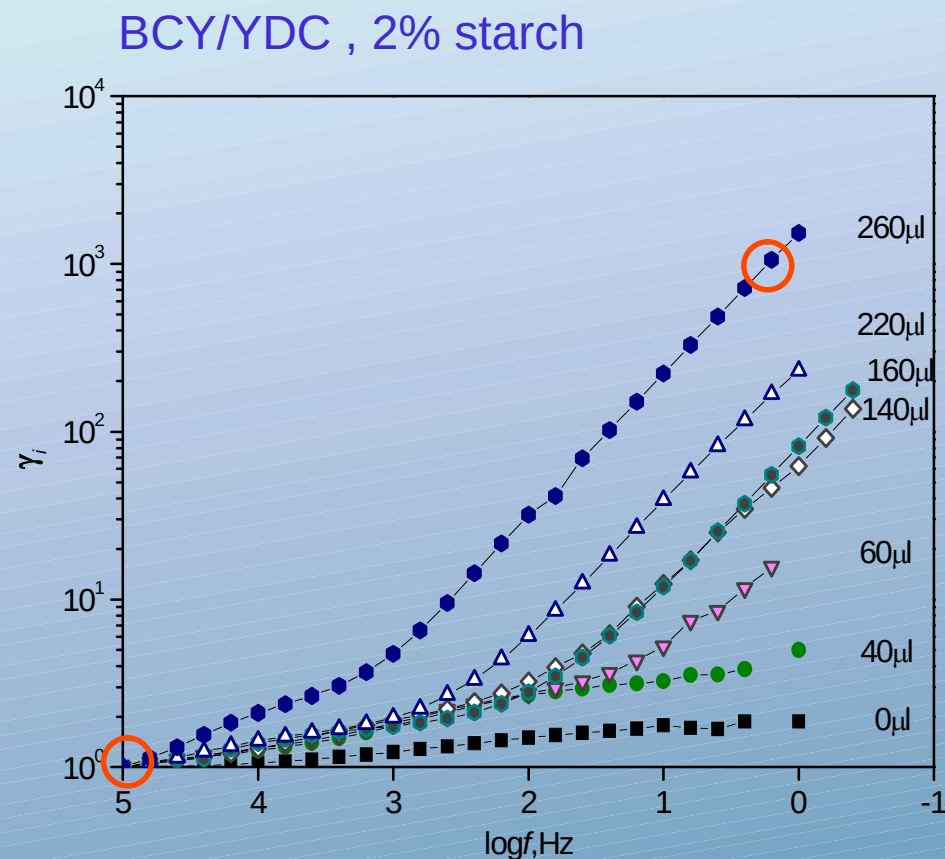
Data Processing



Coefficient of gigantic enhancement definition

$$\gamma_i = \frac{C'_i}{C'_0}$$

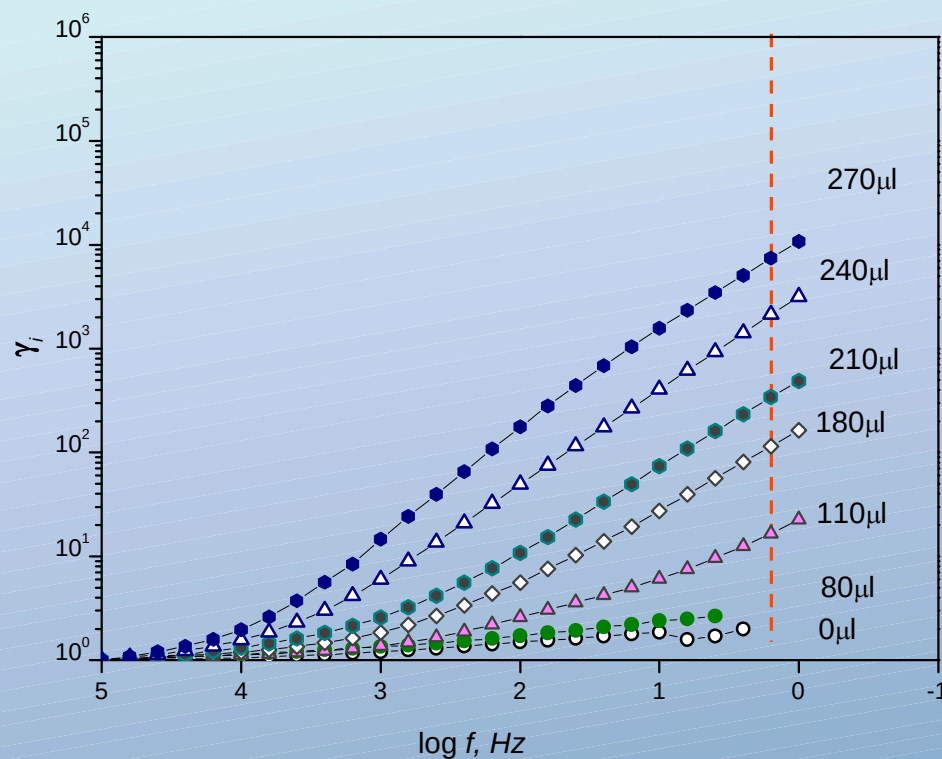
Coefficient of gigantic enhancement γ_i is defined as the ratio between the capacitance C'_i at a given frequency ω_i and C'_0 - the capacitance at the highest measured frequency.



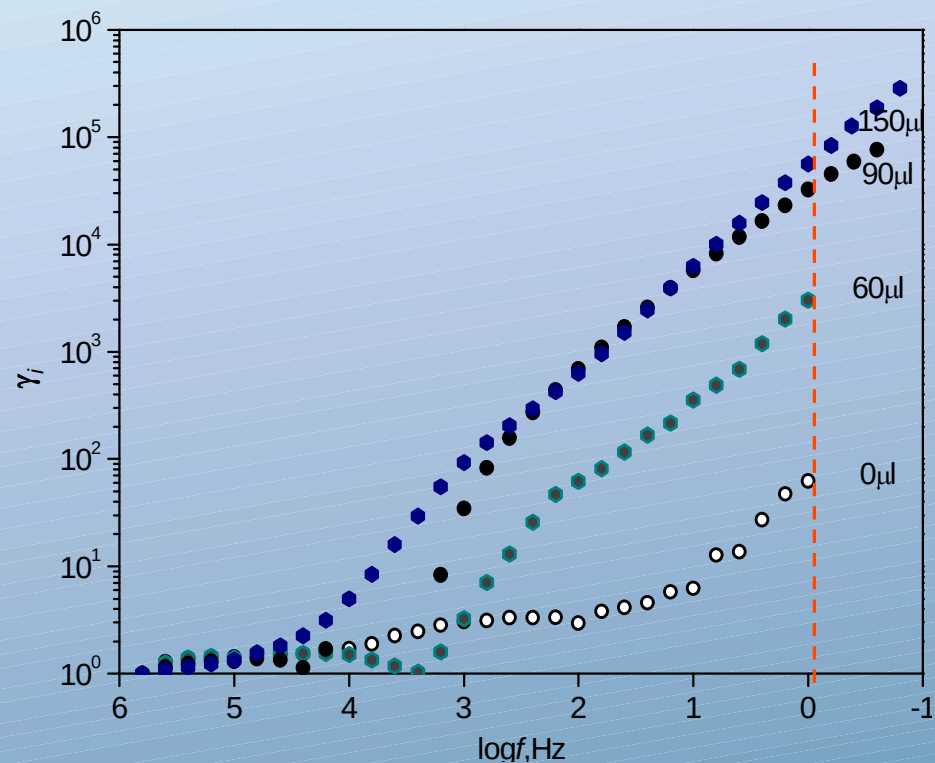


Coefficient of gigantic enhancement - influence of the matrix

BCY/YDC, 2% graphite



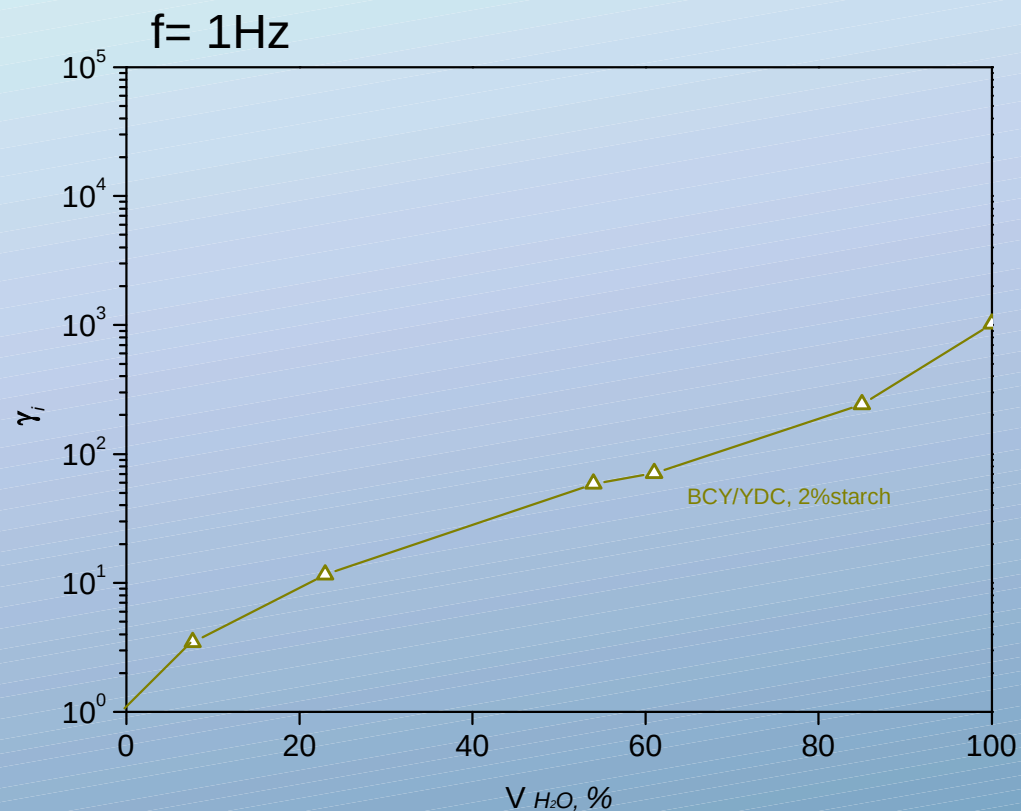
BCY, 2% graphite





Single-frequency analysis

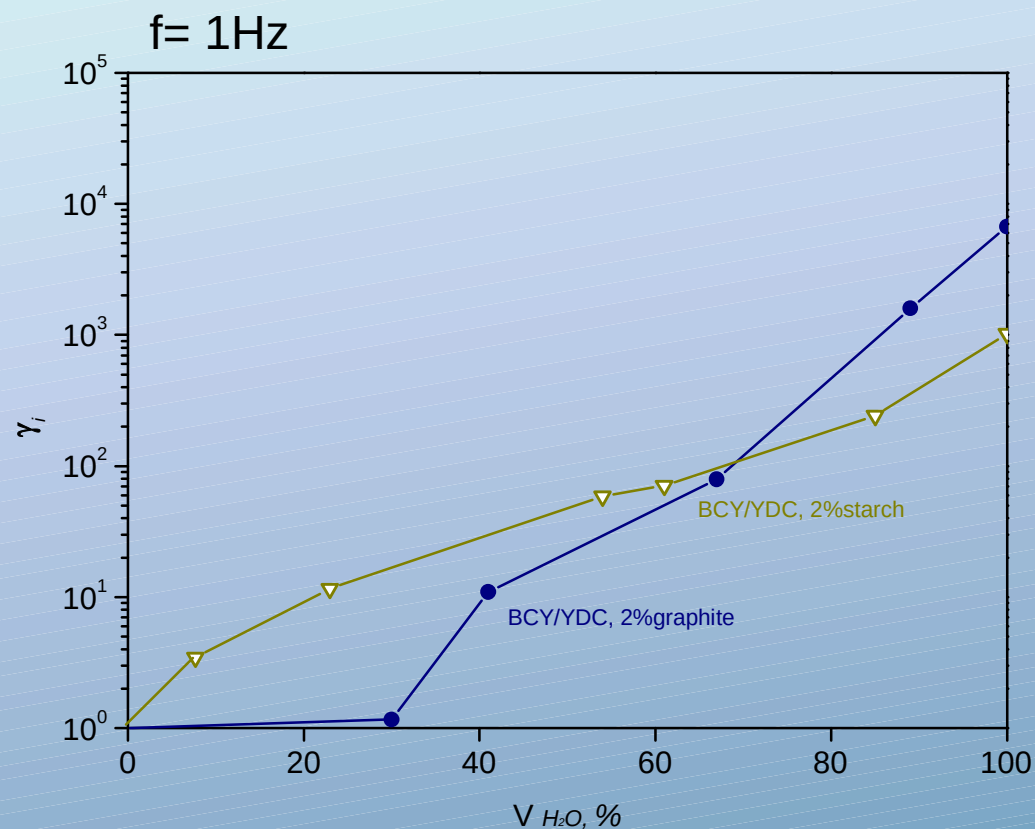
Measured data of the single-frequency analysis which gives the relation between C' (expressed as γ_i) and the quantity of added water for a chosen single frequency.





Single-frequency analysis

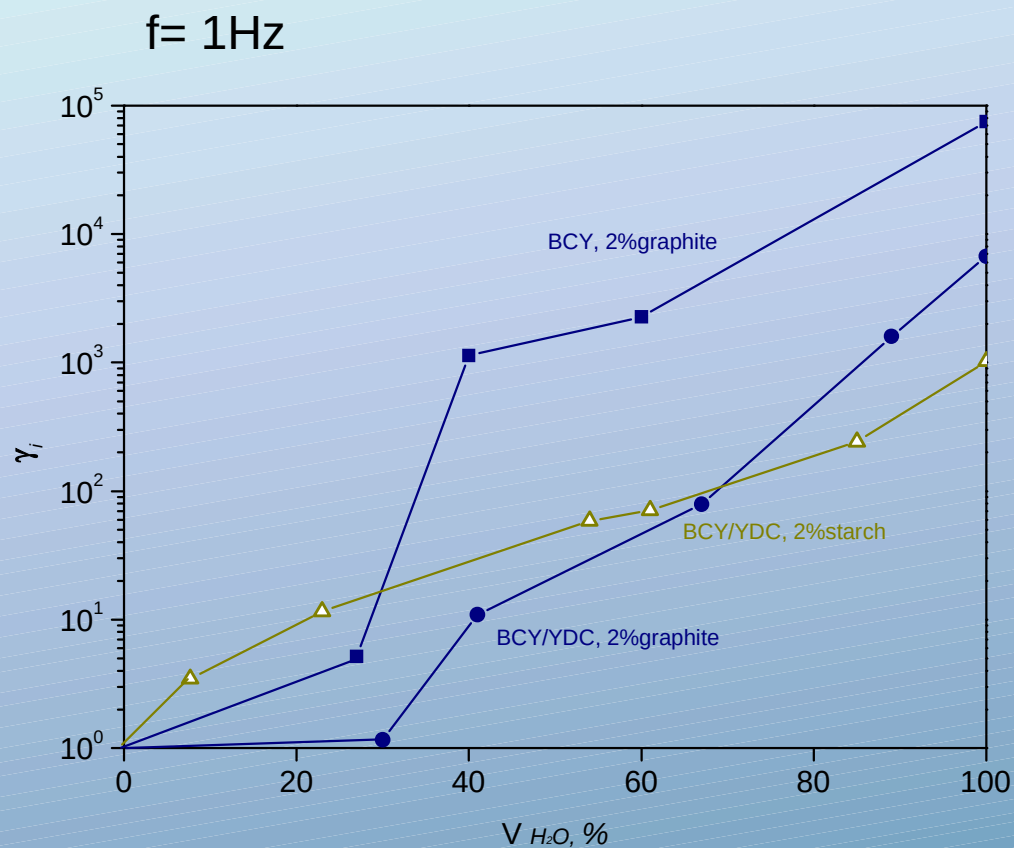
Presentation of the measured data of the single-frequency analysis which gives the relation between C' (expressed as γ_i) and the quantity of added water for a chosen single frequency.





Single-frequency analysis

Presentation of the measured data of the single-frequency analysis which gives the relation between C' (expressed as γ_i) and the quantity of added water for a chosen single frequency.





Conclusions

- A new Phenomenon for water in porous solid media is found : Gigantic enhancement of the real component of the permittivity capacitance C' with decreasing frequencies. The obtained experimental results can be explained with hemisorption of water species, followed by formation and self - organization of dipole film that covers the pores surface. The process starts as hydroxylation of the surface, preferably the BCY one, for which the dissociative absorption of water is a natural property.
- The gigantic enhancement of C' for pure BCY15 porous membrane reaches up to 10^5 times at 1Hz; for composite BCY15/YDC15 material this factor is 10^4 .
- The Phenomenon depends also on the type porosity.



Thank you for the attention!