



ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY ANALYSIS IN ELECTRODES FOR REDOX SUPERCAPACITORS

R. G. Duarte^{1,2}, R. Pedro Silva², A. Garcia-Gomez², T. Nguyen², S. Eugénio², T. Moura Silva^{2,3}, M. João Carmezim^{2,4} and M. F. Montemor^{2,5}

¹ Instituto Politécnico de Setúbal, ESTBarreiro, R. Américo da Silva Marinho, 2839-001 Lavradio, Portugal

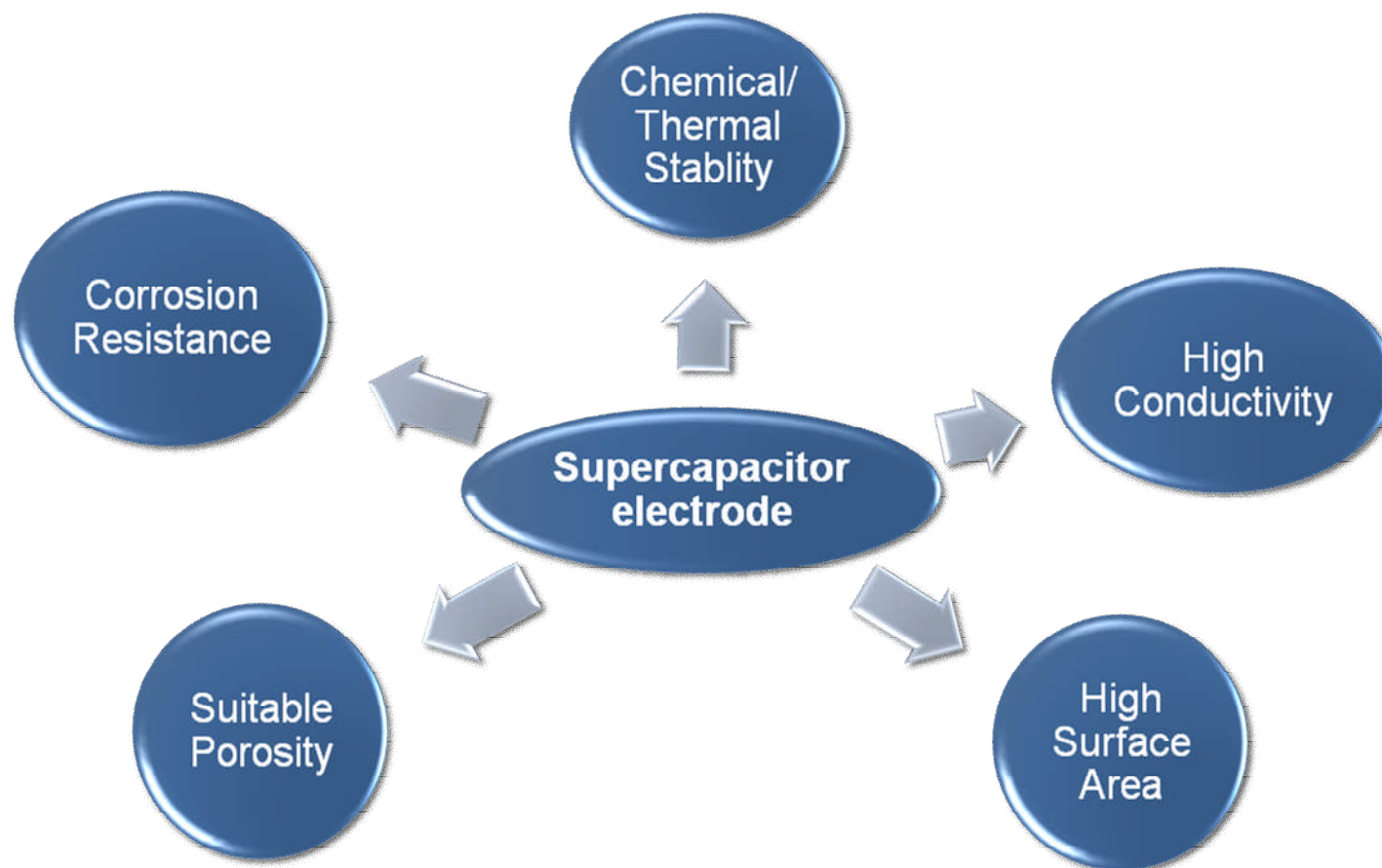
² ICEMS – IST, ULisbon, Av. Rovisco Pais, 1049 – 001 Lisboa, Portugal

⁴ Instituto Politécnico de Setúbal, ESTSetubal, Campus IPS, 2910 Setúbal, Portugal

⁵ Dept. of Chemical Engineering, Instituto Superior Técnico, ULisbon, Lisboa, Portugal

E-mail: raquel.duarte@estbarreiro.ips.pt

INTRODUCTION



The development of new functional materials with high specific capacitances

INTRODUCTION

Transition metal oxides nanostructured films present interesting features for redox supercapacitor electrodes.

Transition metal oxides



- ☐ *High capacitances*
- ☐ Lack of stability
- ☐ Loss of efficiency
- ☐ Increasing resistivity



It is possible to tailor the composition, stoichiometry and structure of oxide mixed to overcome the drawbacks

EXPERIMENTAL

SAMPLES PREPARATION:

Electrodeposition of mixed metal oxides in AISI 304 SS (energy collector)

Co-Ni 3D dendritic nanostructures

- NiCl_2 + CoCl_2 solution + heat treatment

Co-Ni oxide structures

- $\text{Ni}(\text{NO}_3)_2$ + $\text{Co}(\text{NO}_3)_2$ solution

Co-Graphene co-deposited nanostructures

- graphene oxide + $\text{Co}(\text{NO}_3)_2$ solution

EIS MEASUREMENTS:

Equipment's

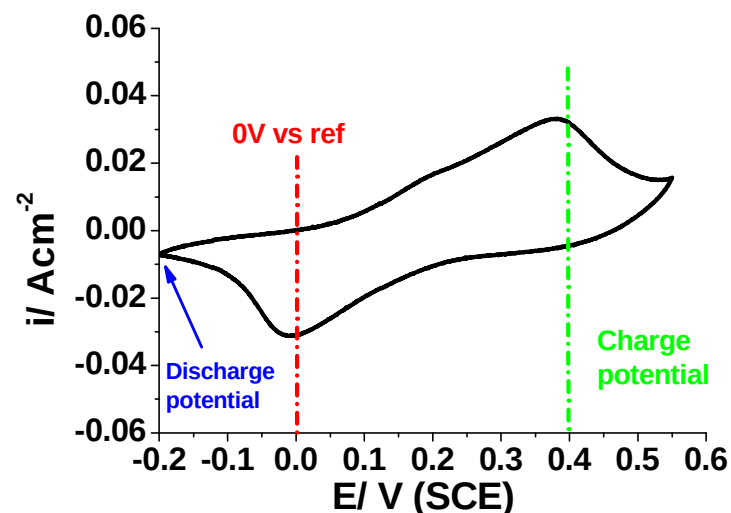
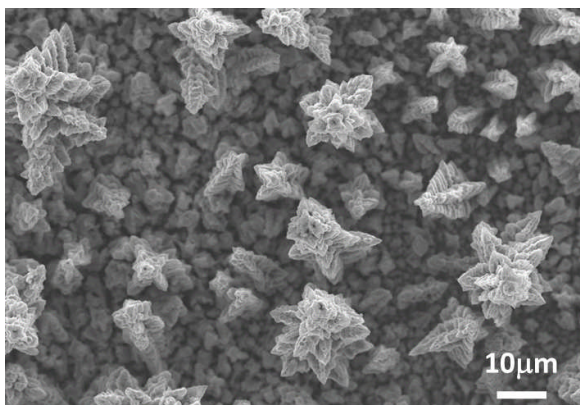
- Ref 600 Gamry Instruments
- Autolab PGSTAT302N

Measurements

- 3-electrode configuration cell
- Amplitude: 10mV rms signal
- Frequency range: 50kHz to 5mHz/20 mHz
- Bias potential : fully charged electrode and fully discharged electrode
- Electrolyte: KOH 1M or NaOH 1M
- WE area: 0.665 cm²

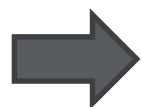
RESULTS AND DISCUSSION

CO-NI 3D DENDRITIC STRUCTURES



Voltamogram do not present rectangular shape typical of double layer charging processes

Redox peaks can be observed



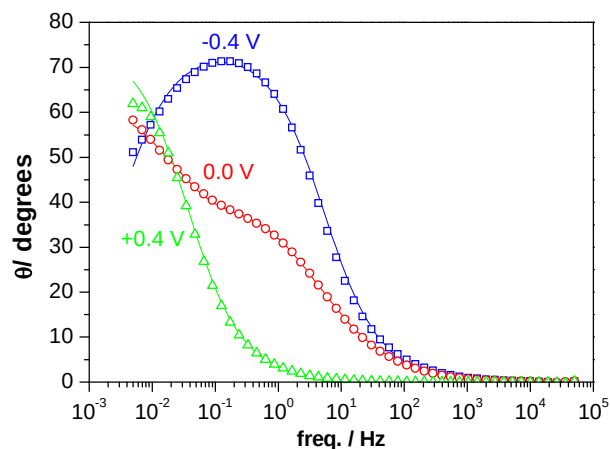
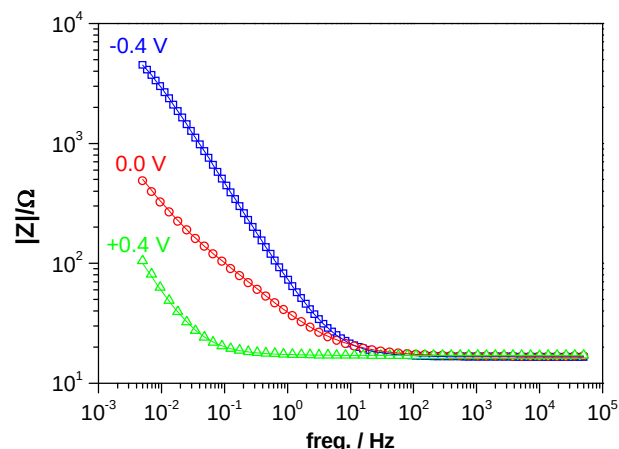
Charge storage mechanism results mainly from faradaic reactions



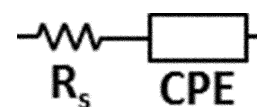
Electrodes display a pseudocapacitive response

RESULTS AND DISCUSSION

CO-NI 3D DENDRITIC STRUCTURES



CHARGED-CONDITION (0.4V vs. SCE)

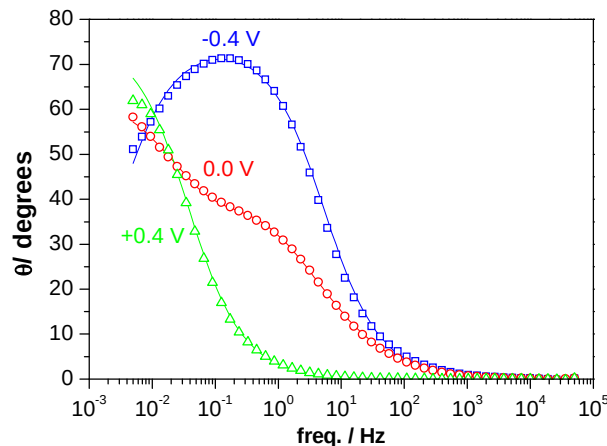
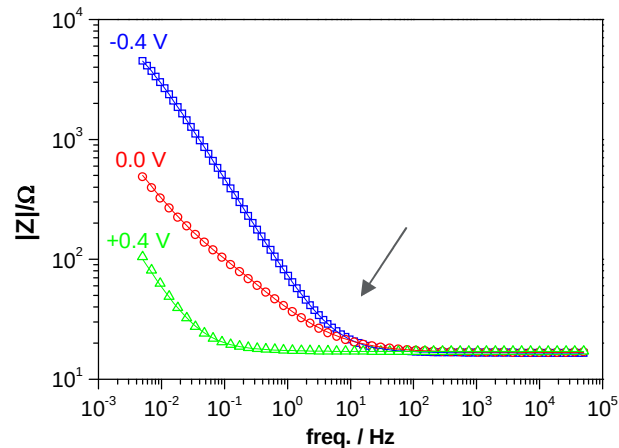


- High frequency resistance (electrolyte resistance)
- CPE element accounting for capacitive response (result of film heterogeneities).

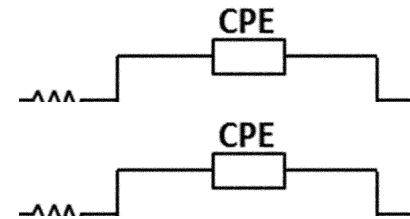
The admittance of the CPE and n presents high value indicating an electrode charge-state.

RESULTS AND DISCUSSION

CO-NI 3D DENDRITIC STRUCTURES



DISCHARGED-CONDITION (-0.4v VS ESC)

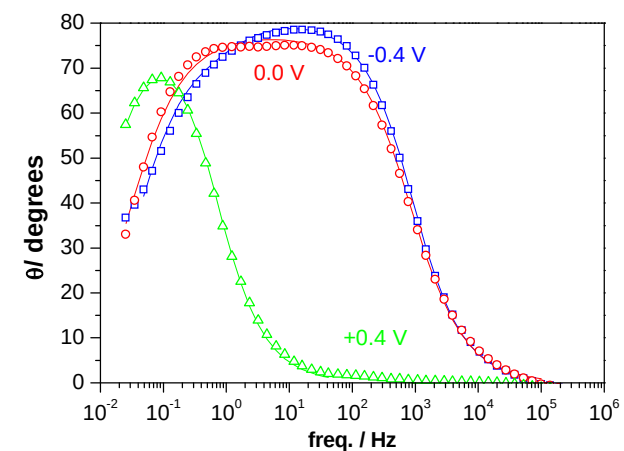
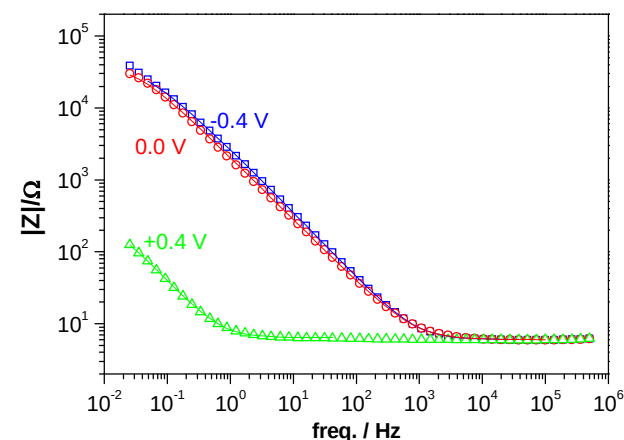
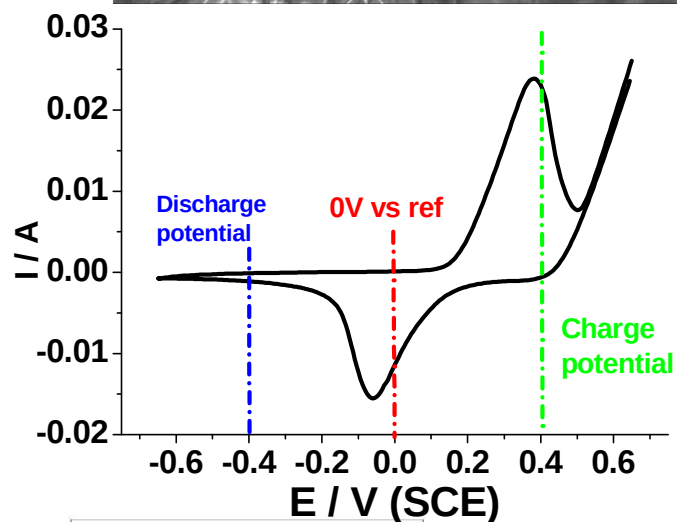
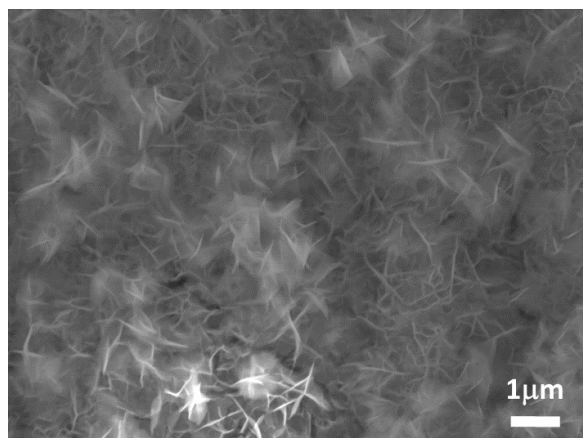


Addition of a resistor accounting for the film resistance and a Warburg accounting for diffusional effects, reflecting the behavior of a porous electrochemically active oxide/electrolyte interface

The admittance of the CPE presents lower values indicating an electrode discharge-state.

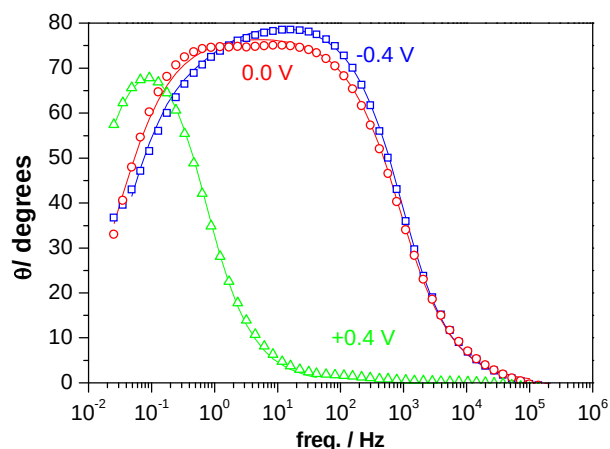
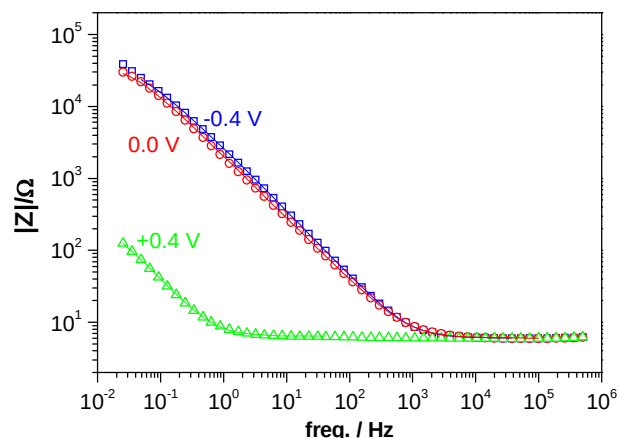
RESULTS AND DISCUSSION

CO-NI OXIDE STRUCTURES

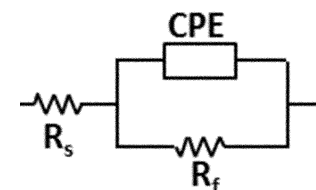


RESULTS AND DISCUSSION

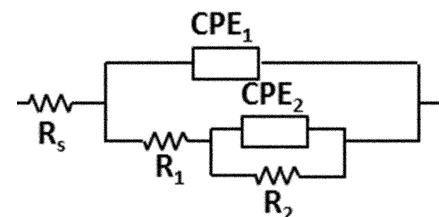
CO-NI OXIDE STRUCTURES



CHARGED-CONDITION (0.4V vs. REF)



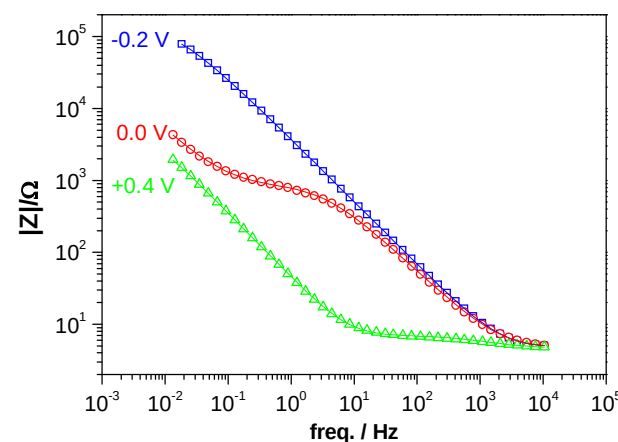
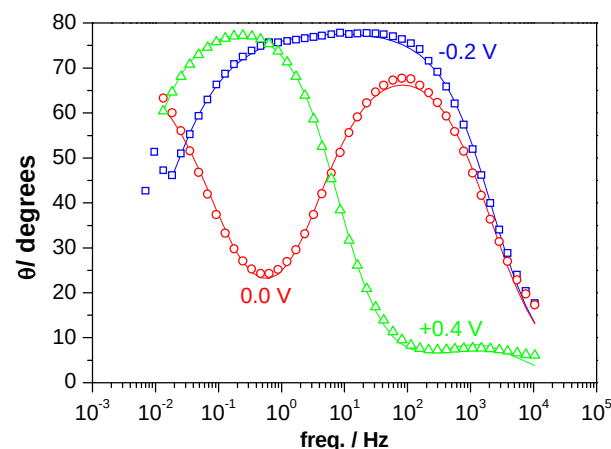
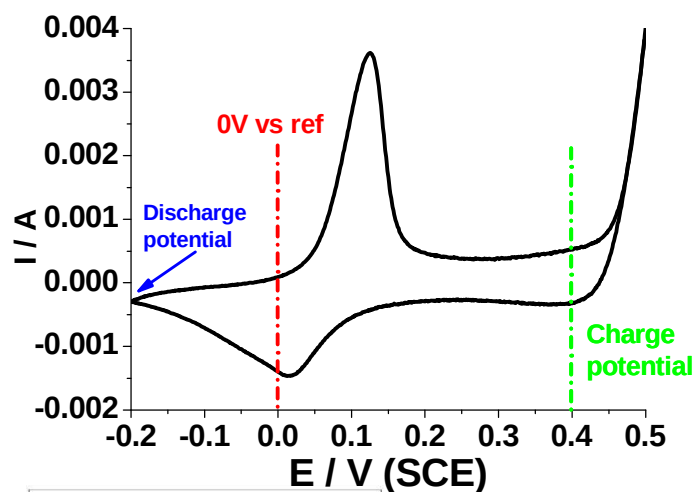
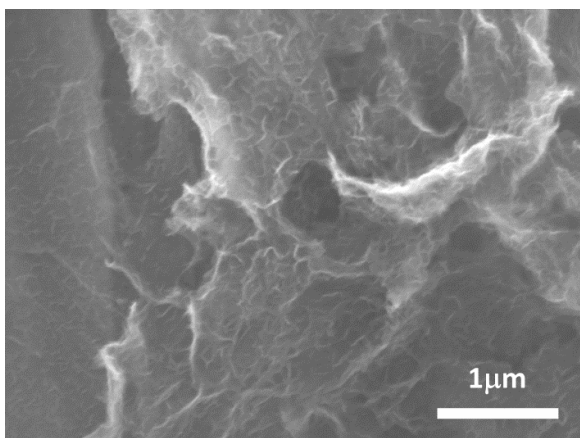
DISCHARGED-CONDITION (-0.4V vs. REF)



Similar behavior to Co-Ni 3D dendritic structures (but slightly more resistive system than the previous case)

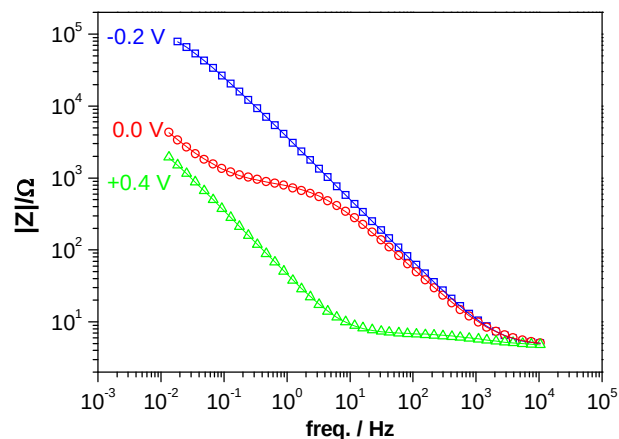
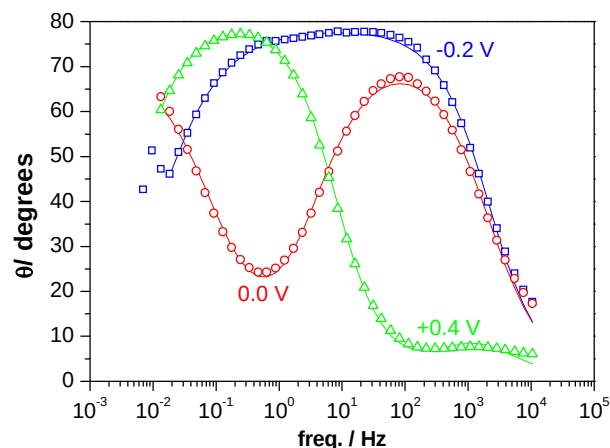
RESULTS AND DISCUSSION

CO-GRAPHENE CO-DEPOSITED NANOSTRUCTURES

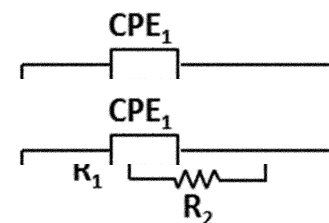


RESULTS AND DISCUSSION

CO-GRAPHENE CO-DEPOSITED NANOSTRUCTURES



CHARGE AND DISCHARGED-CONDITION



EIS reveals two time constants, probably associated to oxidation and reduction of graphene oxide [1].

-High frequency time constant can be associated with reduced oxide graphene.

-Low frequency time constant can be associated with graphene oxide and cobalt present in the nanostructure.

[1] E. Casero, A. M. Parra-Alfambra et. Al, *Electrochem. Communications*, 2012, 20, 63

CONCLUSIONS

- The results showed that the EIS response is sensitive to the potential applied to the electrode, *i.e.* on the electrode state-of-charge.
- The electrochemical response of the electrodes was detailed by fitting the EIS spectra. For this purpose, various electrochemical circuits are proposed.
- The results show that EIS is a powerful tool to extract information regarding the capacitive and resistive contributions of the metallic oxides and graphene-containing composite electrodes under different applied potential.

ACKNOWLEDGEMENTS

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