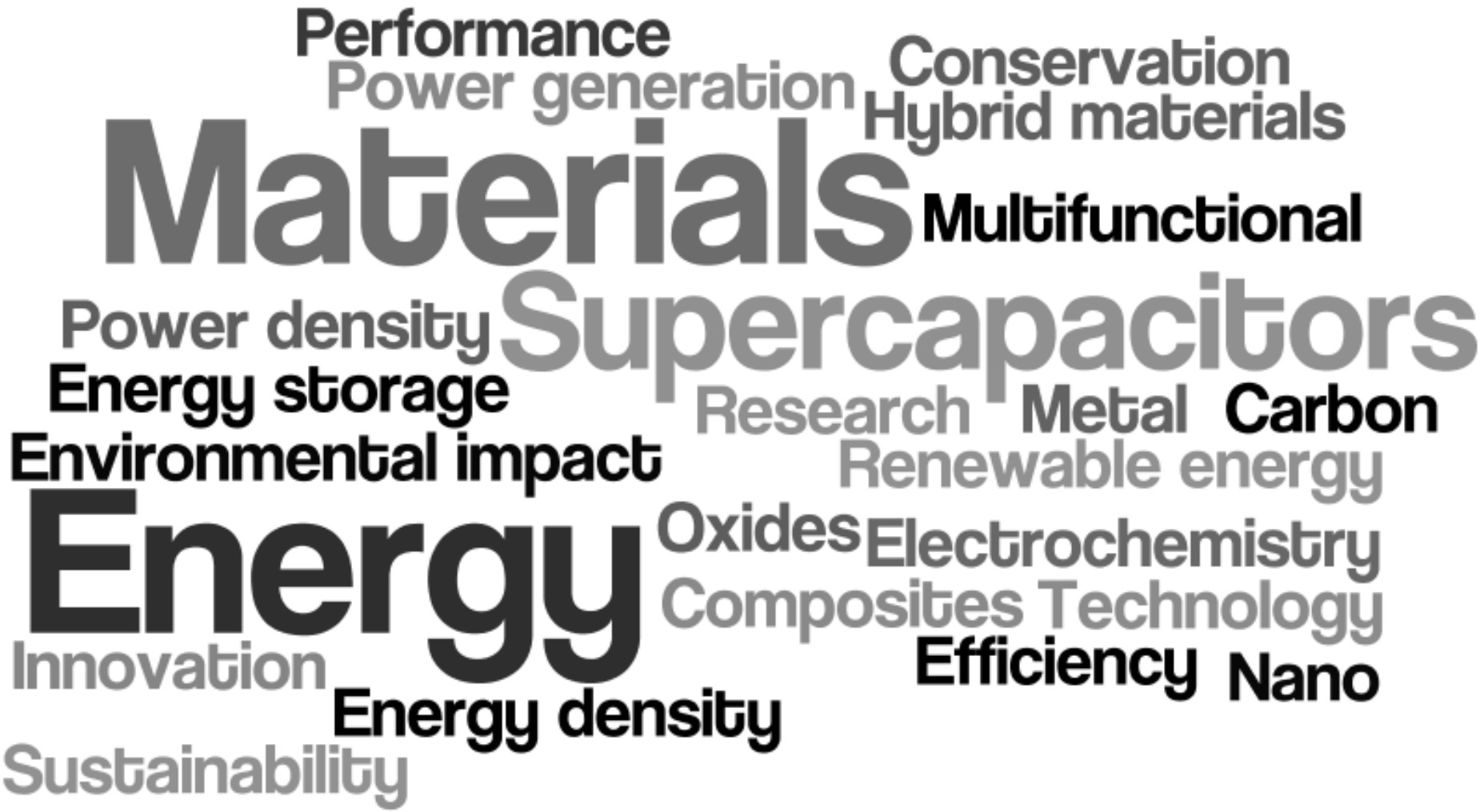
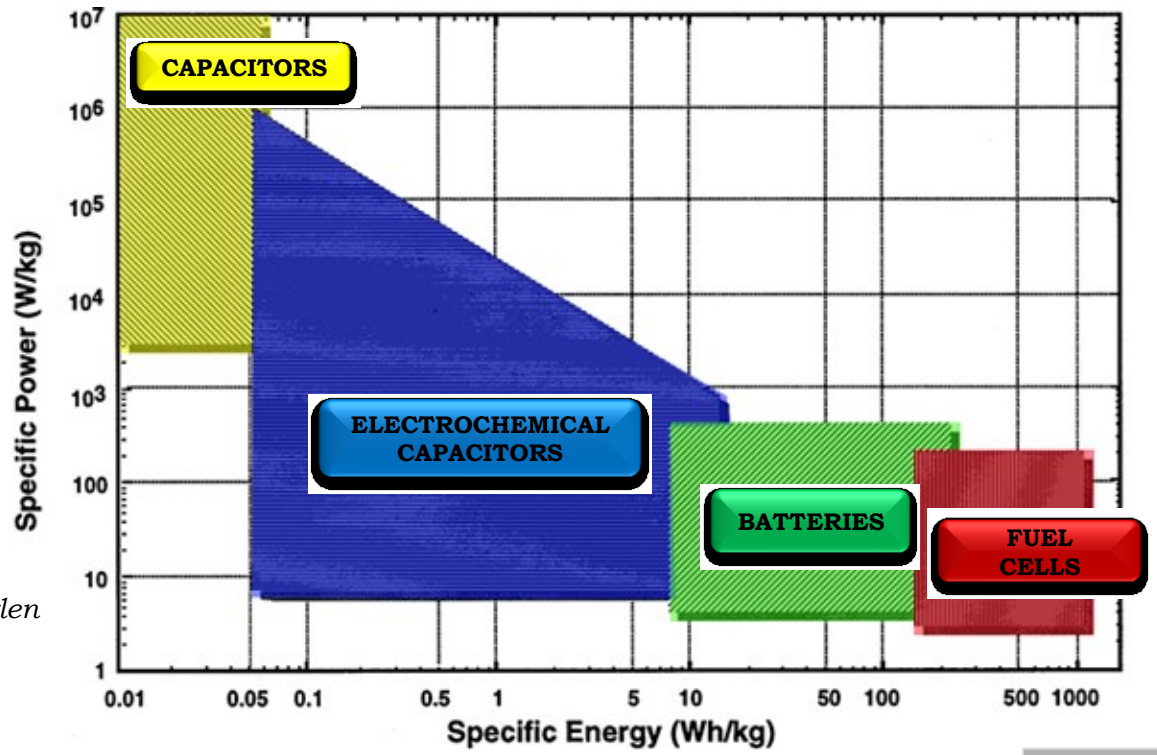
Development of transition metal films and their application as electrodes for supercapacitors

S. EUGÉNIO, R.P. SILVA,
M.T. SILVA, M.F. MONTEMOR, M.J. CARMEZIM

2012 INTERNATIONAL WORKSHOP ON ENVIRONMENT AND ALTERNATIVE ENERGY
Greenbelt, Maryland – December 4 – 7, 2012


Performance
Power generation
Conservation
Hybrid materials
Materials
Multifunctional
Power density
Supercapacitors
Energy storage
Research
Metal
Carbon
Environmental impact
Renewable energy
Energy
Oxides
Electrochemistry
Composites
Technology
Innovation
Efficiency
Nano
Energy density
Sustainability

Electrochemical supercapacitors: **Characteristics**



Source: R. Kotz , M. Carlen Electrochimica Acta 45 (2000) 2483–2498

Capacitors

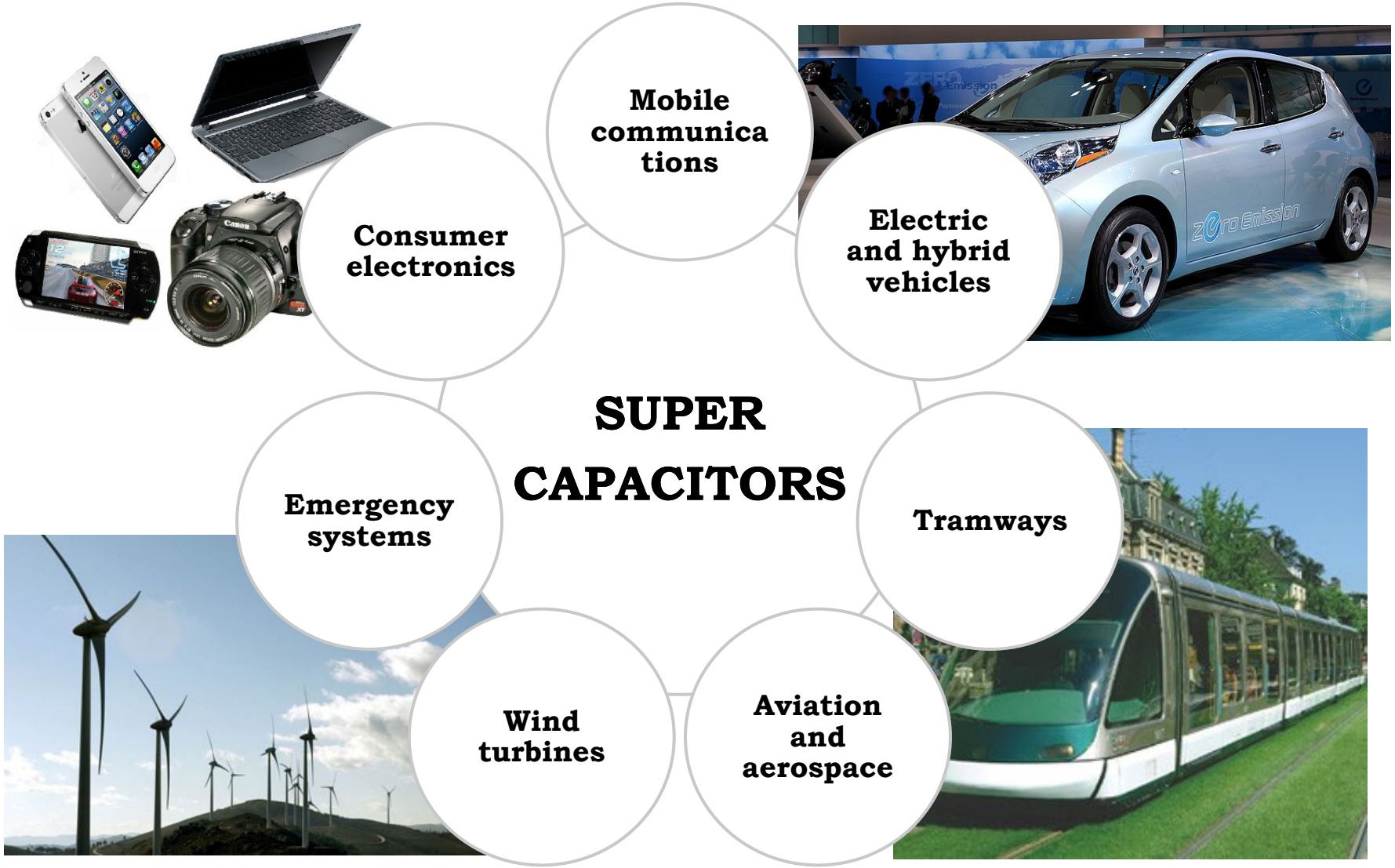
Supercapacitors

Rechargeable batteries

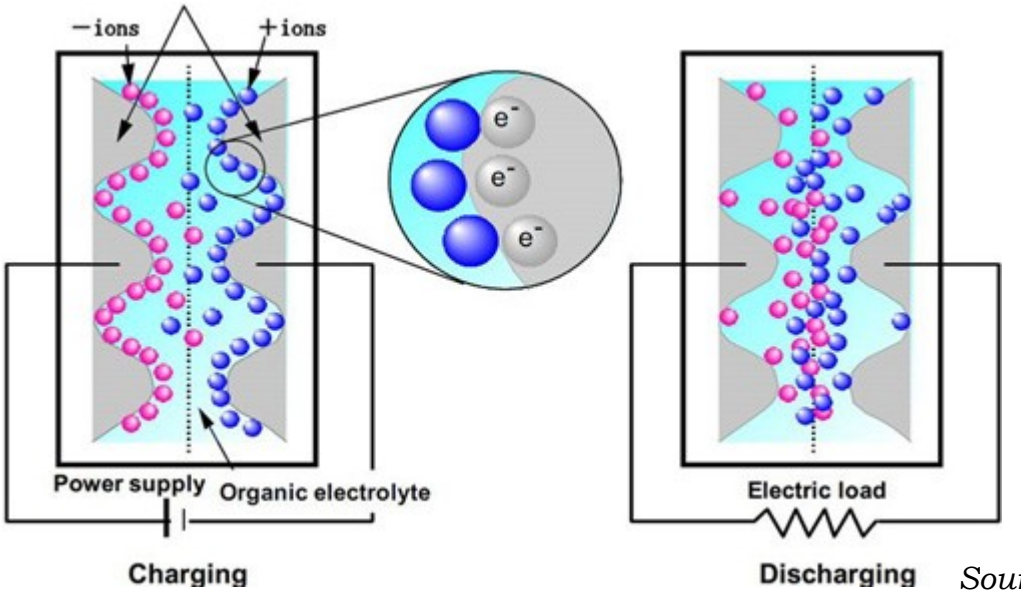
Storing small amount for short time
Fast delivery

Major storage for long time
Slow delivery

Electrochemical supercapacitors: **Applications**



Electrochemical supercapacitors: **Mechanisms**



Source: capacitor.com.hk

Electrical double-layer capacitors

Based solely on double-layer formation
(Capacitance arises from charge separation at an electrode/electrolyte interface)

Redox electrochemical capacitors

Based on reversible faradaic reactions (charge-transfer pseudocapacitance arises from reversible Faradaic reactions occurring at the electrode surface)

Electrodes for electrochemical supercapacitors: **Properties**

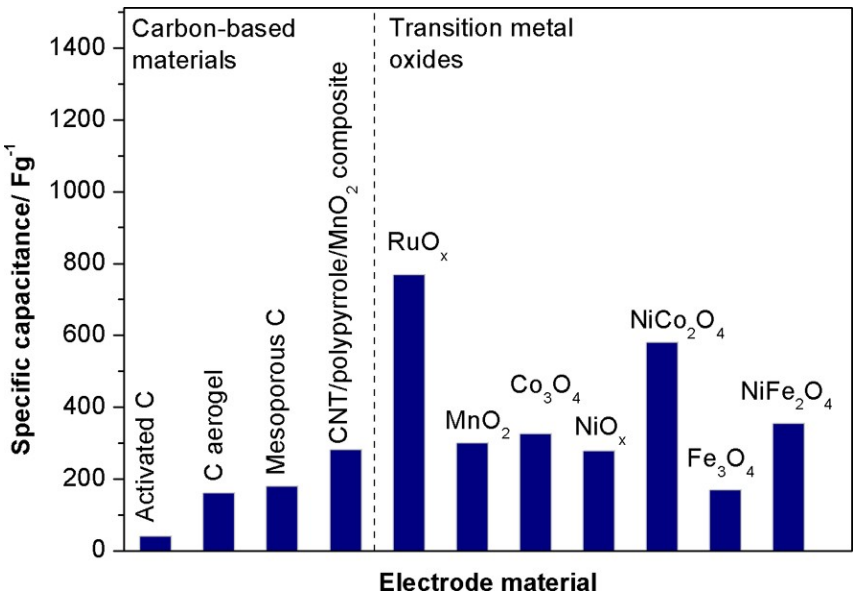
High specific surface area (enhanced porosity)	→	More active sites
Suitable pore-size distribution (pore network and length)	→	Facilitate diffusion of ions at high rate
Low internal electrical resistance	→	Efficient charge transport
Enhanced electrochemical and mechanical stability	→	Good cyclic performance

Electrodes for electrochemical supercapacitors: **Materials**

Carbon –based materials
High surface area
High thermal stability

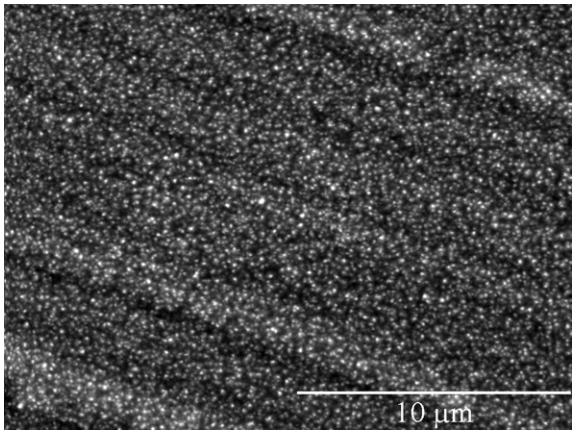
Conducting polymers
Relatively high specific capacitance
Reduced cycling stability

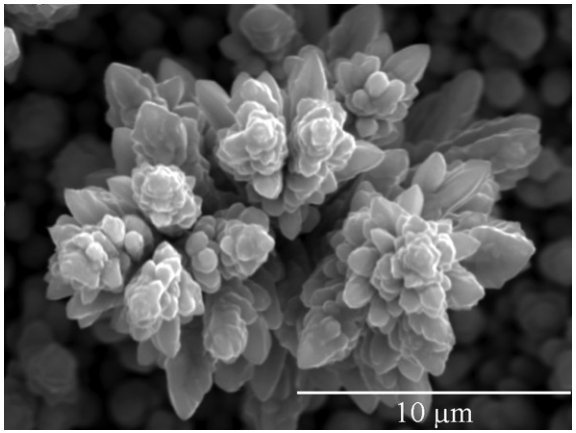
Metal oxides
High specific capacitance
Low resistance

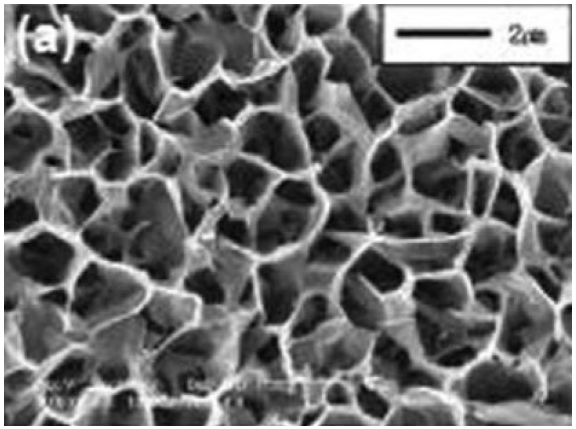


Source: C.D. Lokhande et al. Current Applied Physics (2011) 11 255-270

Electrodes for electrochemical supercapacitors: **Electrodeposition**







Versatile, low cost process

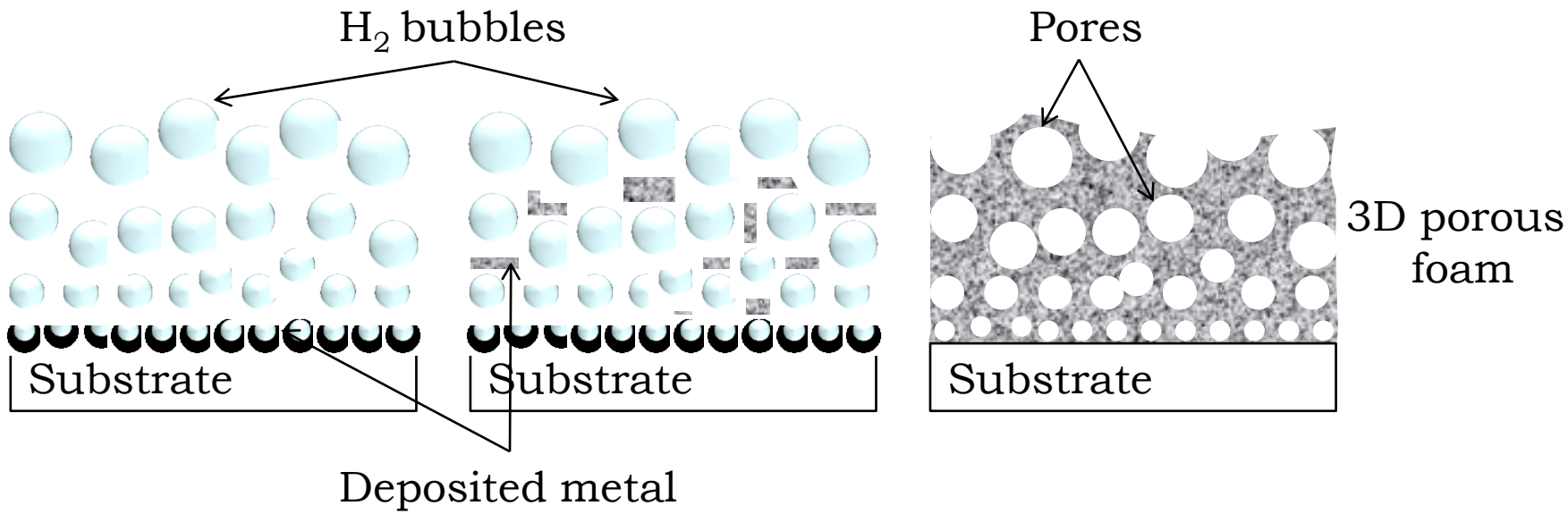
Electrolyte composition
+
deposition parameters

Wide range of morphologies

K. W. Chung et al., Electrochem. Solid-State Lett., 2005, 8, A259

Electrodeposition of Ni-Cu and Ni-Co-Cu films by hydrogen bubble template

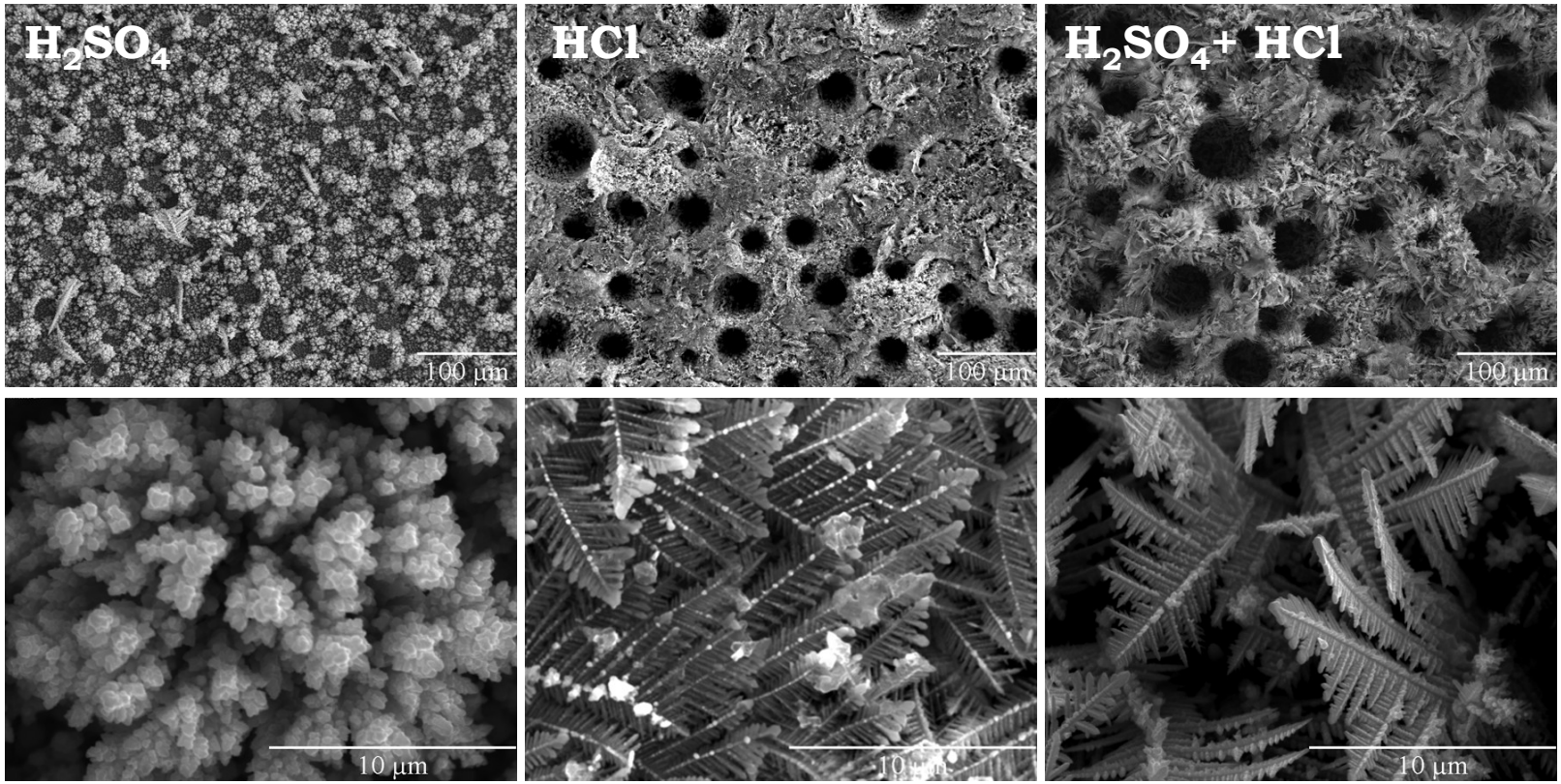
Electrodeposition method: **hydrogen bubble template**

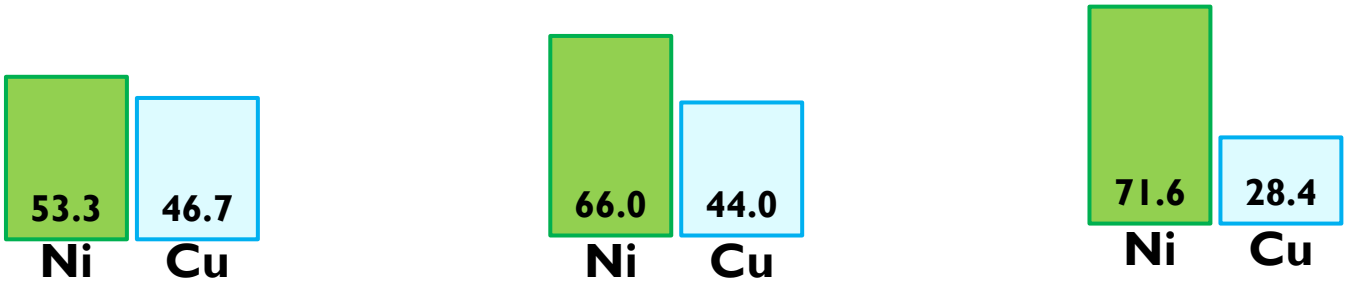


Hydrogen bubbles act as a dynamic template for the formation of the nanostructured foam

H. Shin and M. Liu Chemistry of Materials 16 (2004)5460-5464

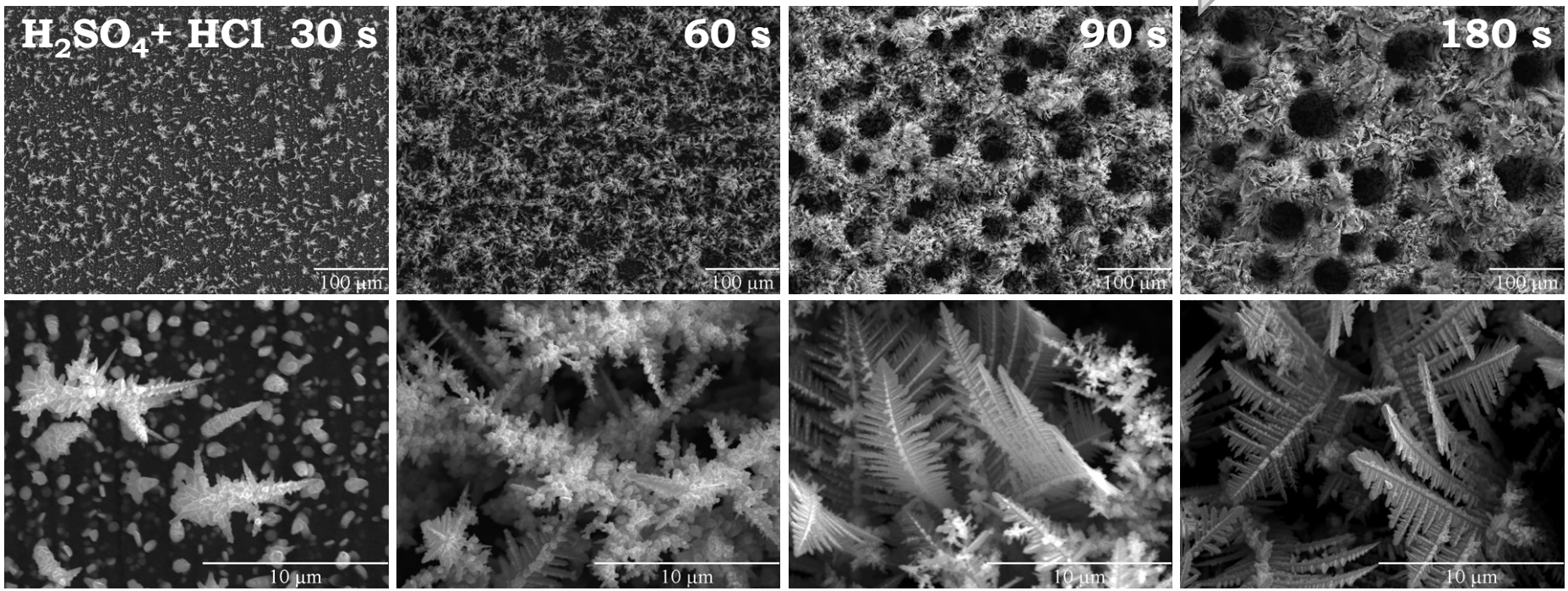
Electrodeposition of Ni-Cu films: **Electrolyte composition**

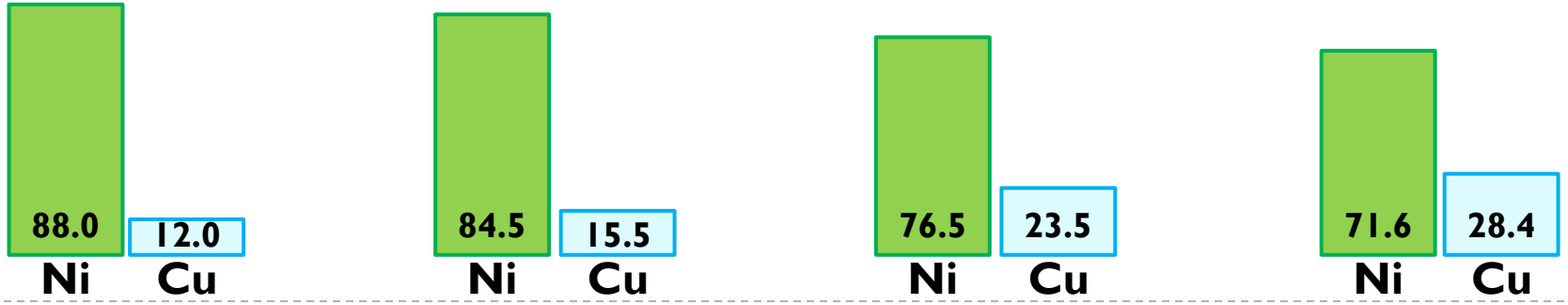




Electrodeposition of Ni-Cu films: **Deposition time**

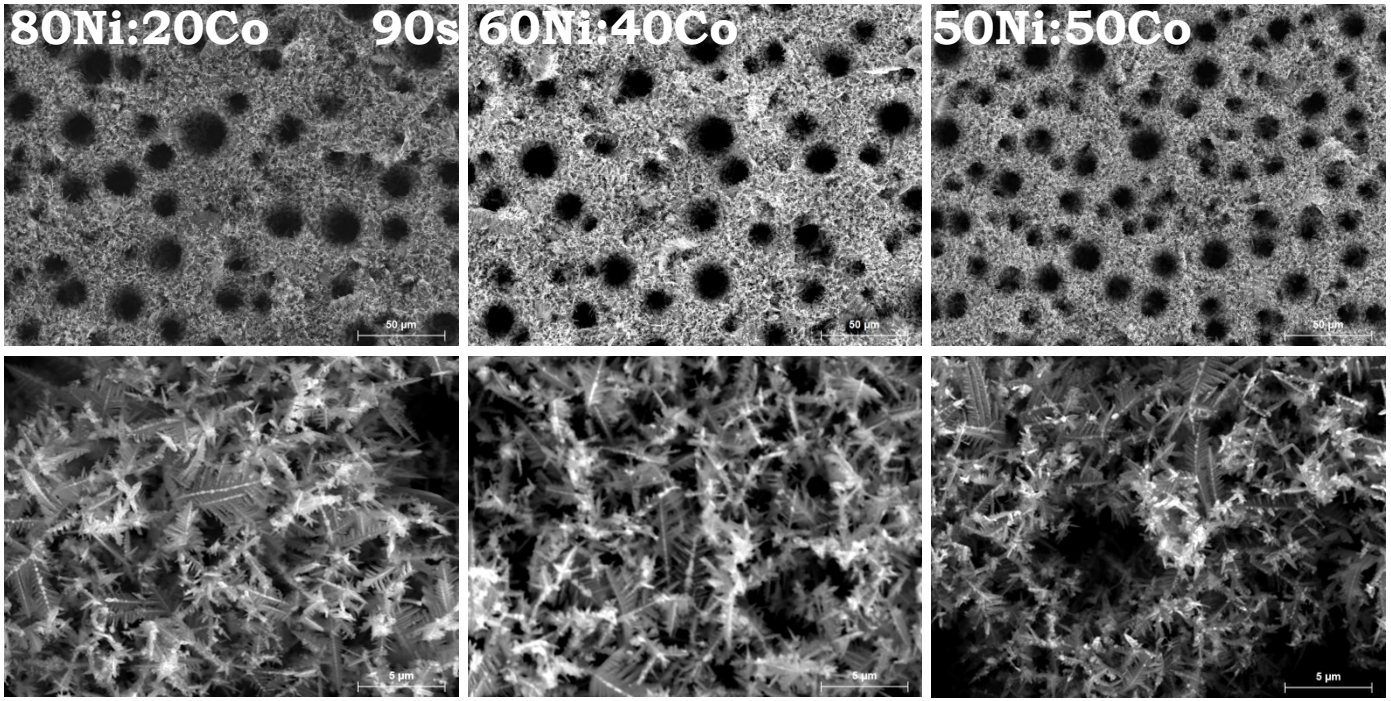
Increasing deposition time

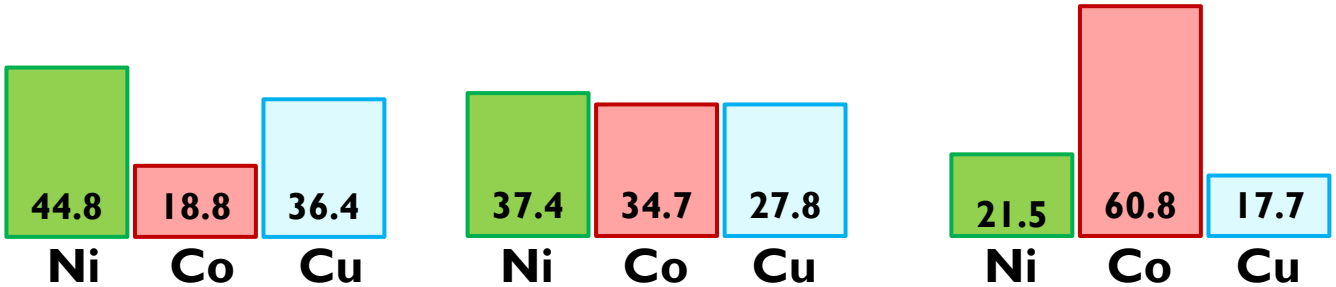




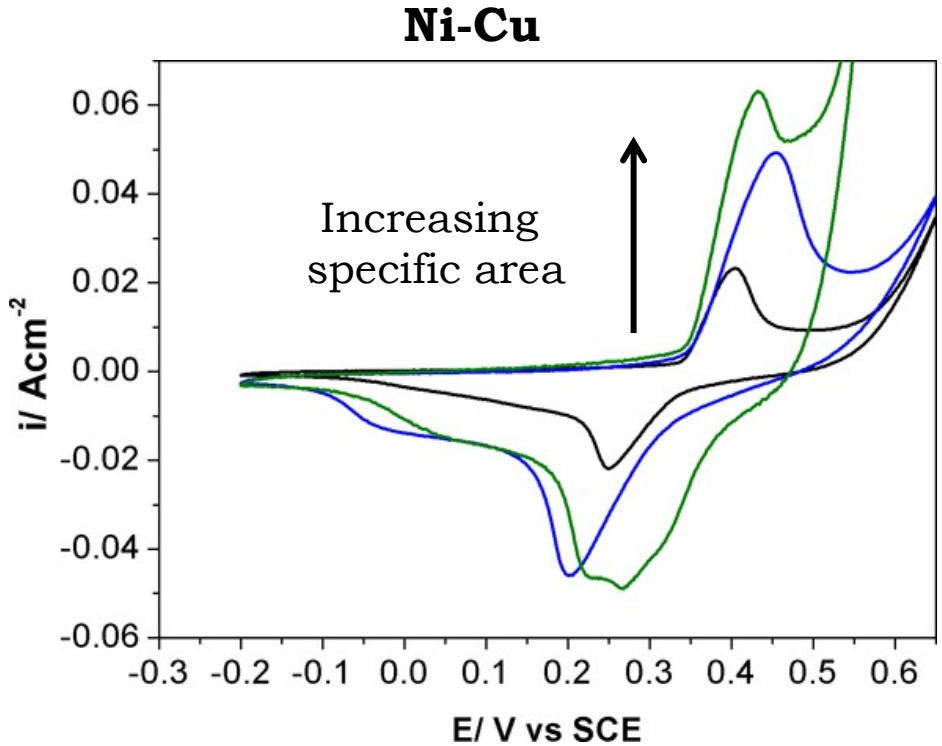
Electrodeposition of Ni-Co-Cu films: **Electrolyte composition**

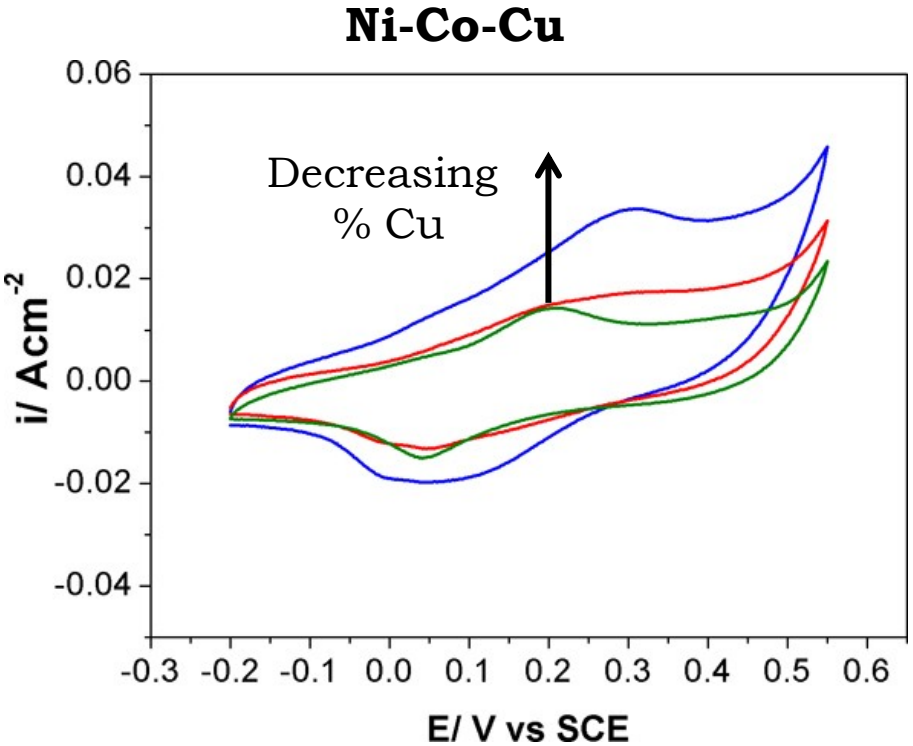
Decreasing Ni content in the electrolyte





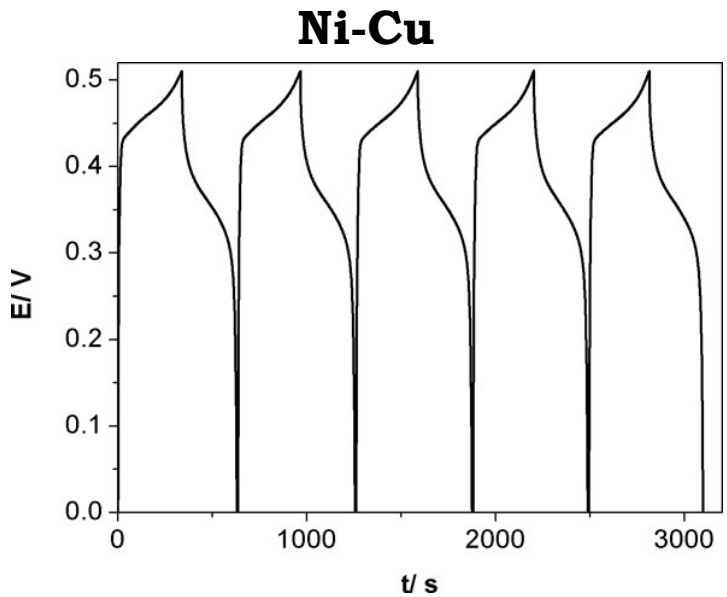
Ni-Co-Cu films:
Cyclic voltammetry in 1M KOH

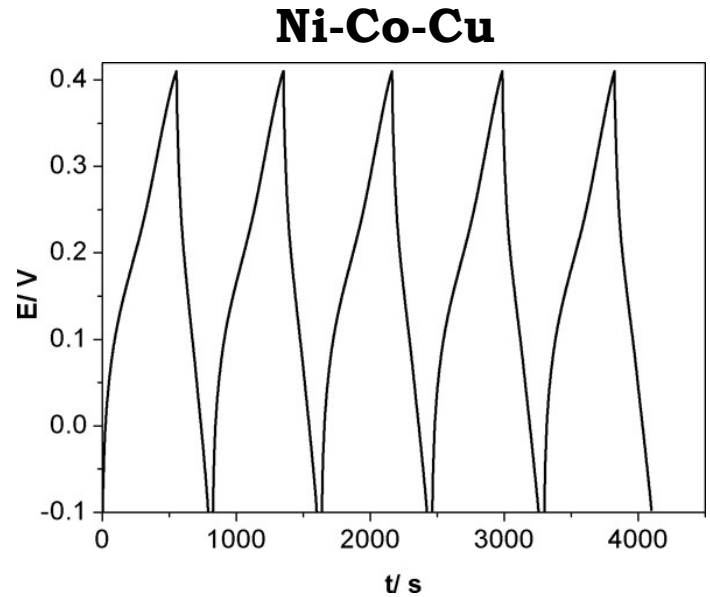


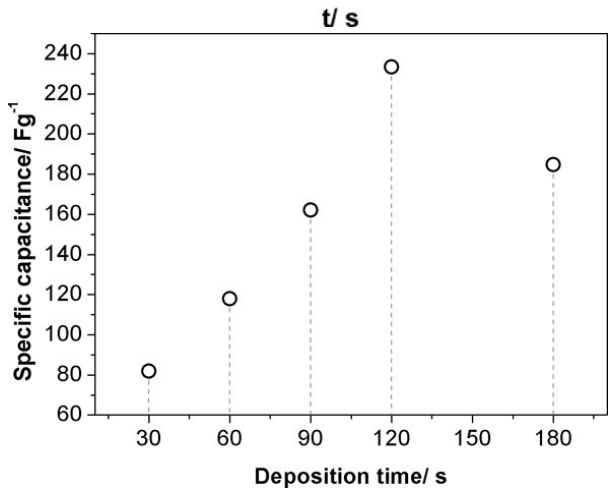


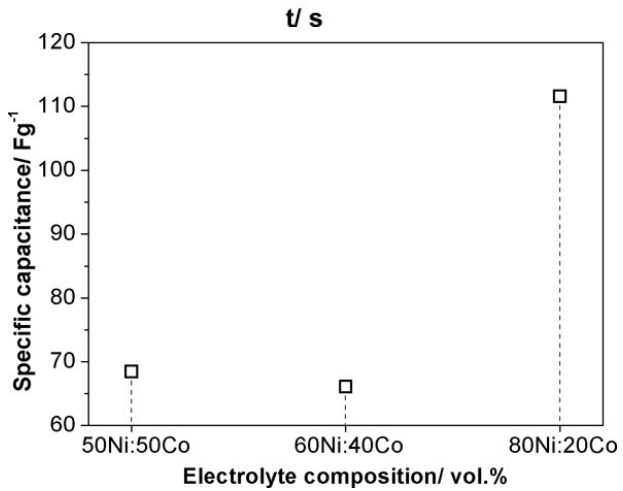
Reduction/ oxidation peaks typical of pseudocapacitance

Ni-Co-Cu films:
Charge-discharge curves in 1M KOH









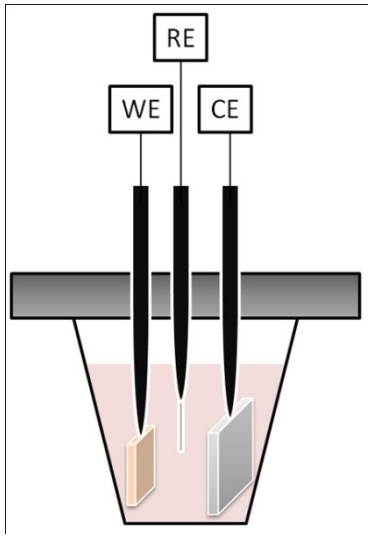
Electrodeposition of Ni-Co dendritic films

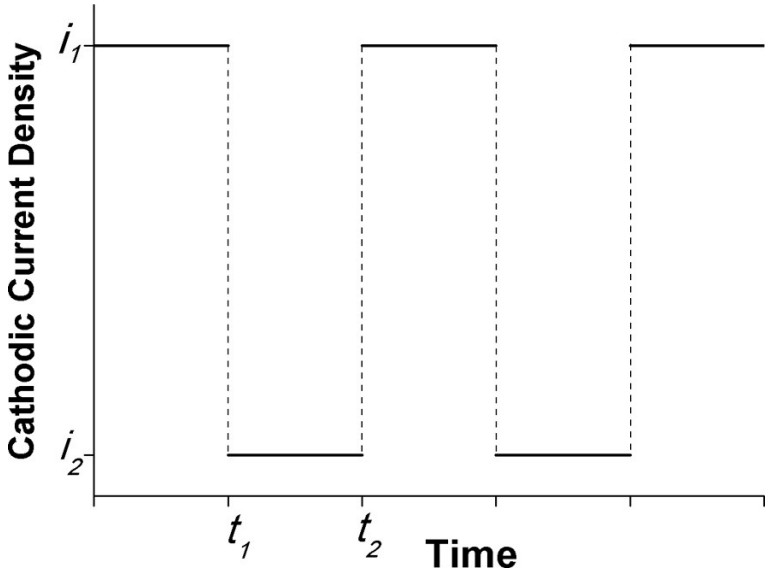
- Portuguese Patent pending, PT106470, 2012.

-R. P. Silva, S. Eugénio, T. M. Silva, M. J. Carmezim and M. F. Montemor J. Phys. Chem. C, 2012, 116 (42), pp 22425–22431. DOI: 10.1021/jp307612g

- Aword in a portuguese contest in materials Science.

Electrodeposition method: **pulsed cathodic deposition**





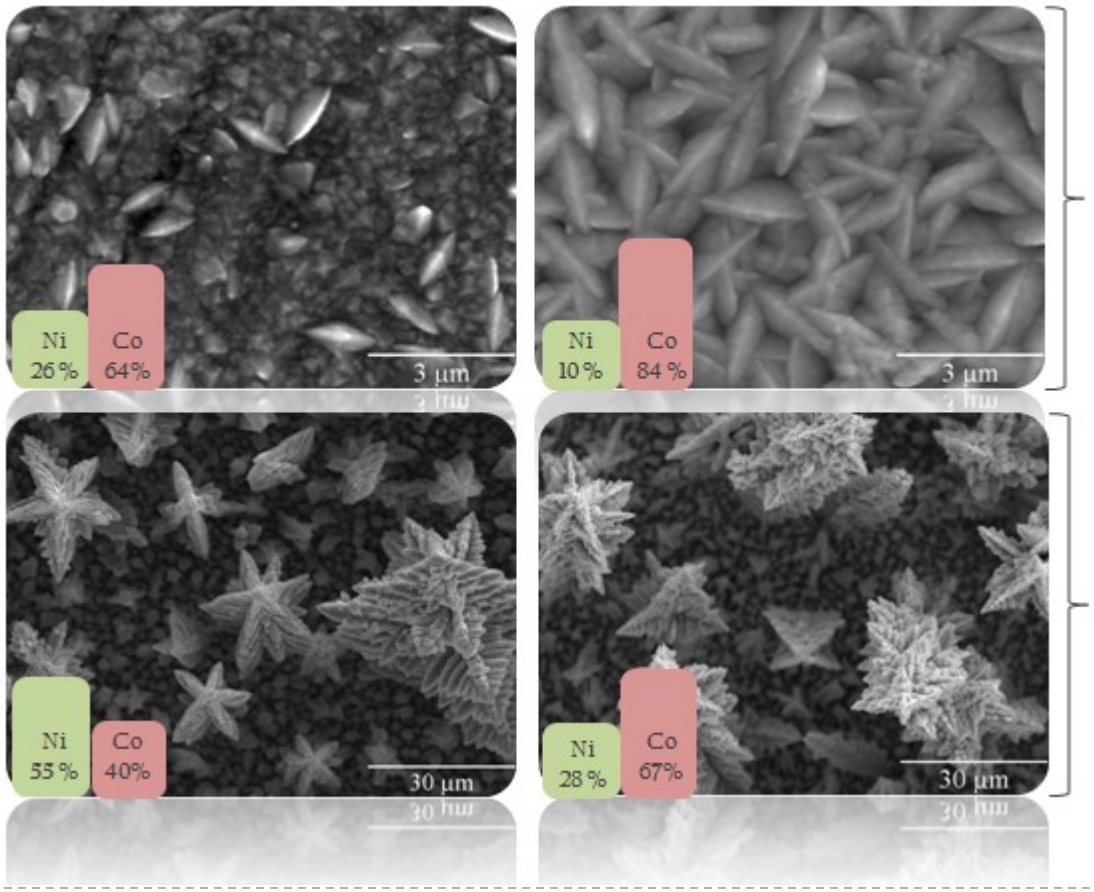
Cathodic deposition of Ni-Co from aqueous electrolytes on stainless steel substrates

Electrodeposition of Ni-Co films: **Deposition parameters**

Different Ni/Co ratio in electrolytic solution

Electrodeposition parameters

Ni/Co = 60/40 Ni/Co = 30/70

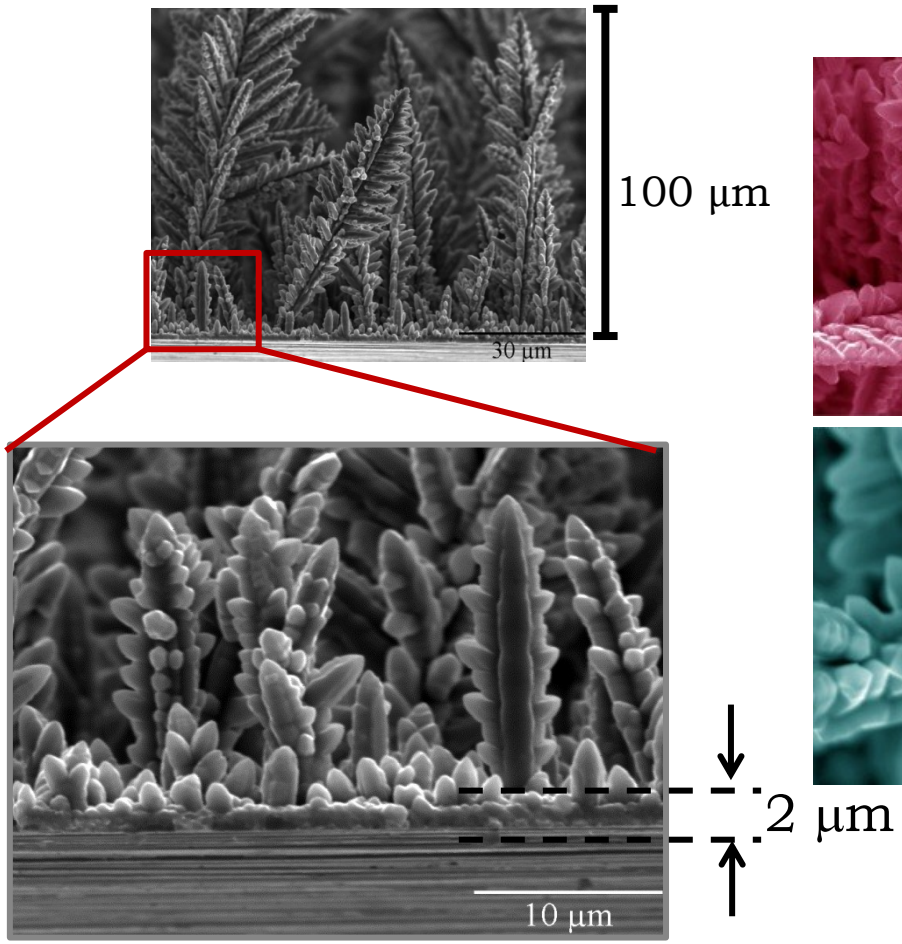


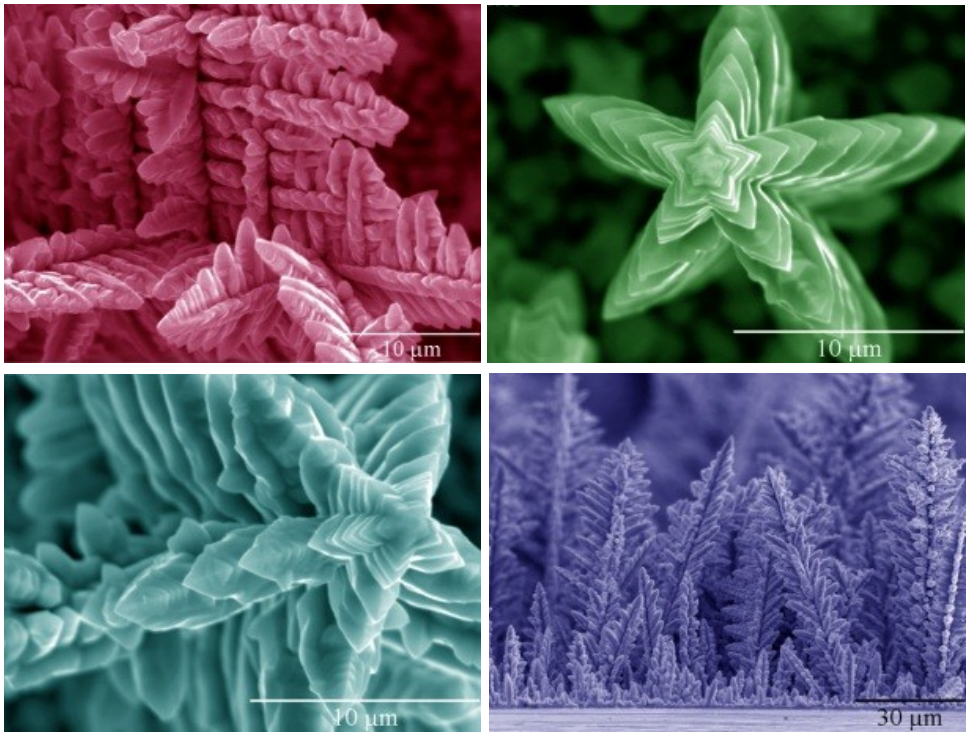
i_1 = -3 mA cm^{-2}
i_2 = -5 mA cm^{-2}

Different applied current density

i_1 = -3 mA cm^{-2}
i_2 = -20 mA cm^{-2}

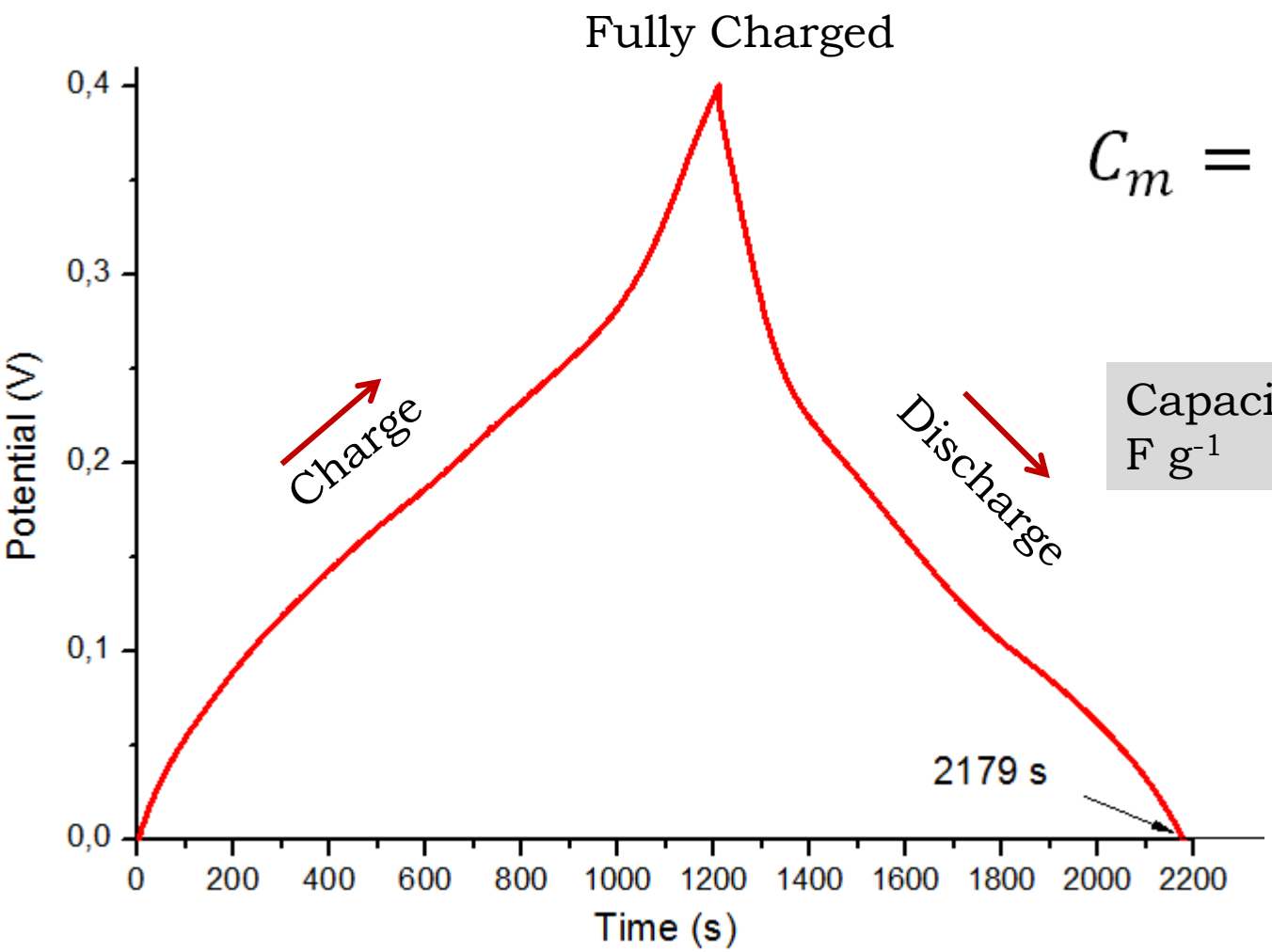
Electrodeposition of Ni-Co films: **Dendritic struture**





Cross-section images of Ni-Co film

Ni-Co films:
Charge-discharge curves in KOH



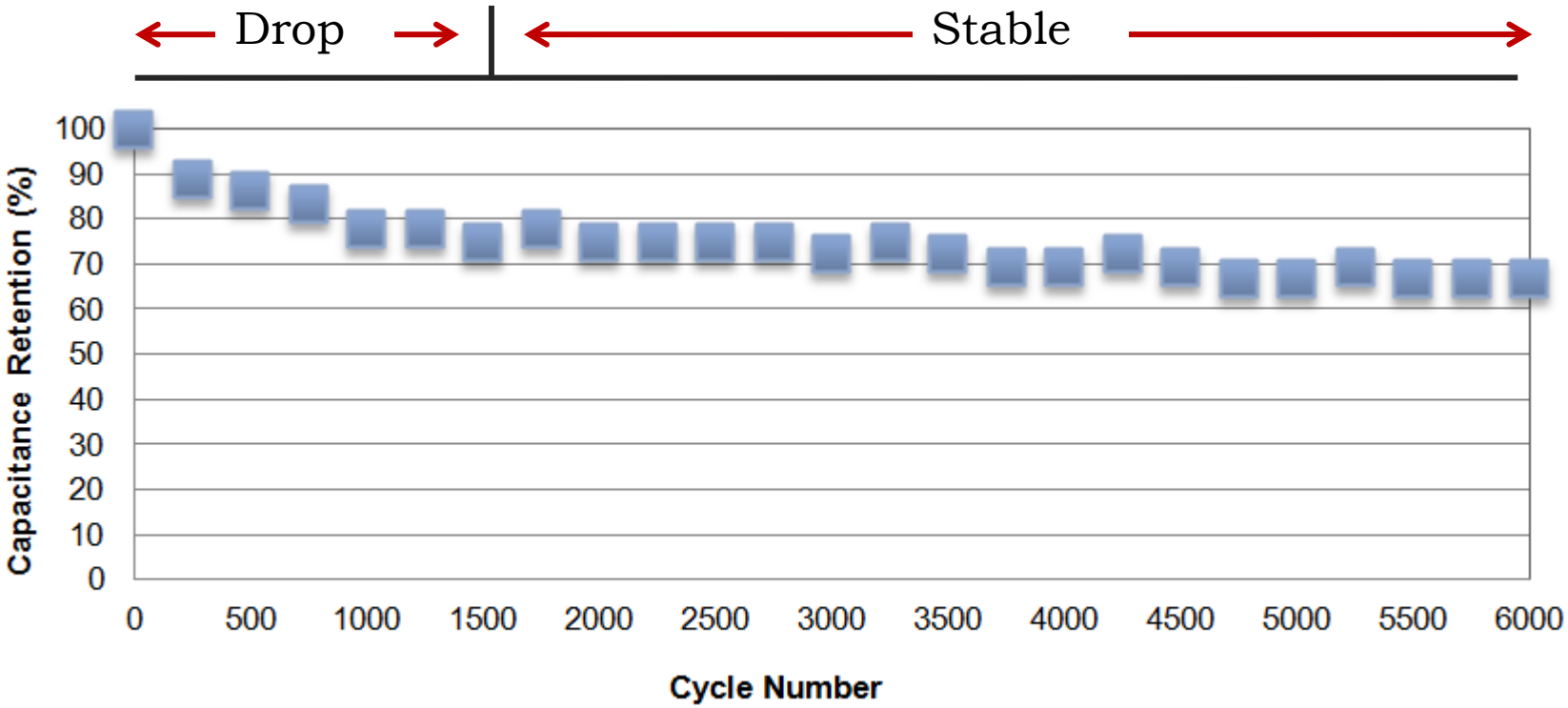
$$C_m = \frac{I_d \times \Delta t}{\Delta V \times m}$$

Capacitance = 369 F g^{-1}

Charge-discharge curves of the Ni-Co film electrode in 1 M KOH solution at a galvanostatic current density of 1 mA cm^{-2}.

Ni-Co films:
Cycle stability in KOH

Almost 70% of specific capacitance remained after 6 thousand cycles.



Dependence of discharge specific capacitance on the charge-discharge cycle numbers.

Conclusions

- Electrodeposition is an effective method for the production of new materials with 3D architectures for supercapacitor electrodes
- Electrodeposition using the dynamic hydrogen bubble template allows the formation of Ni-Cu and Ni-Co-Cu porous foams with a dendritic structure.
- The electrochemical behavior of the foams depends on their surface area and chemical composition, in particular, the Cu content.
- The specific capacitance is higher in Ni-Cu foams where a maximum value of 238 F g - 1 is achieved.
- A new approach consisting on applying a square current waveform in the cathodic domain was successfully applied for the electrodeposition of Ni-Co films. This method has proved to be effective to fabricate a continuous film over which 3D Ni-Co dendrites with highly ramified branches and open porous structures were grown.
- Electrochemical tests confirm these nanostructures show a high capacitance (369 Fg^{-1}) and a capacitance retention of nearly 70% after 6000 cycles.
- Detailed studies on the electrochemical behavior of the present materials are under investigation to enhance their performance.

Acknowledgements

FCT
Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR

cost
EUROPEAN COOPERATION
IN SCIENCE AND TECHNOLOGY

FUNDAÇÃO
LUSO-AMERICANA

C3P
Centro para Prevenção
da Poluição

THANK YOU FOR YOUR ATTENTION!

R.P. SILVA, S. EUGÉNIO

M.T. SILVA, M.F. MONTEMOR, M.J. CARMEZIM