PhD Open Days

Flexible, sustainable & self-healing energy-storage devices:
Design of the next-generation of MnO_2-based pseudocapacitors

Corrosion Science Surface Engineering

Doctoral Program in Chemical Engineering (DEQuim)

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Background and motivation

Novel energy storage pseudocapacitor materials able to repair their own defects are crucial to enhance electrochemical performance and lifetime of electrodes for the next generation of flexible supercapacitors. Novel **MnO_2/N, S-rGO electrodes** tailored for aqueous neutral electrolytes will be developed. Such electrodes will be composed by pH-responsive polymers coating MnO_2/graphene nanoparticles that will detect and repair damaged area '**when**' and '**where**' needed. To the author best knowledge, the study of self-healing MnO_2 (or other redox material) electrodes with pH-active polymers for energy storage applications has not been reported, which reflects the scientific challenge of this work.

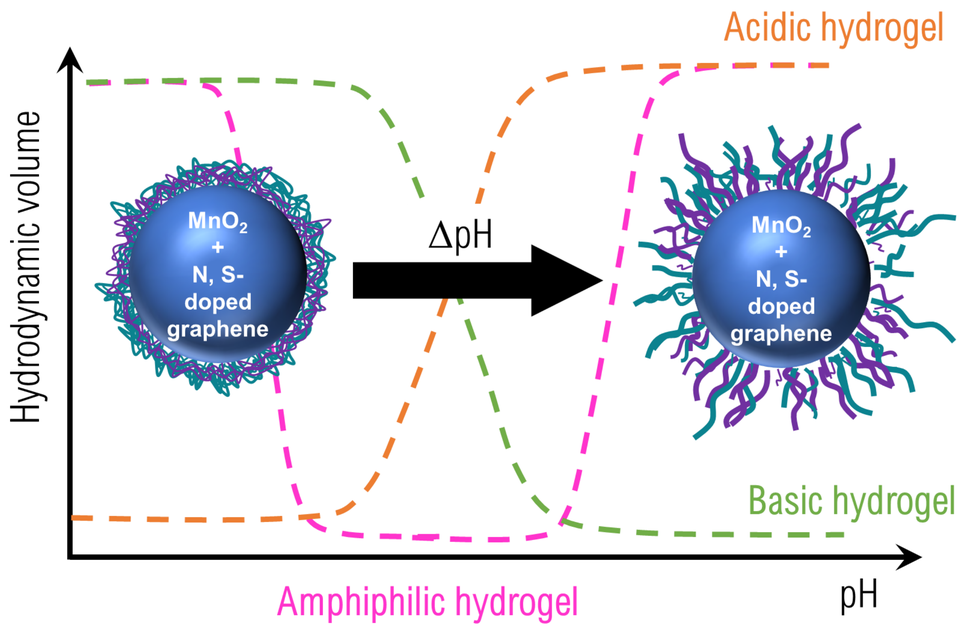

Figure 2: Mechanism of ON/OFF of stimuli-responsive amphiphilic polymeric-based shells with incorporated MnO_2 material.

CURRENT PROBLEM

MnO_2 materials have been significantly studied over the years, thanks to their pseudocapacitive response that is extremely attractive for fast response devices with increased energy density.

However, in neutral aqueous solutions, MnO_2-based electrodes are susceptible to several problems, particularly **deep discharge** and **overcharge cycling** that limit the device performance (Figure 1). Such processes are assigned to electrochemical stress of the material, and are characterized by the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) that induce a local pH change accompanied by the decline of the MnO_2 activity.

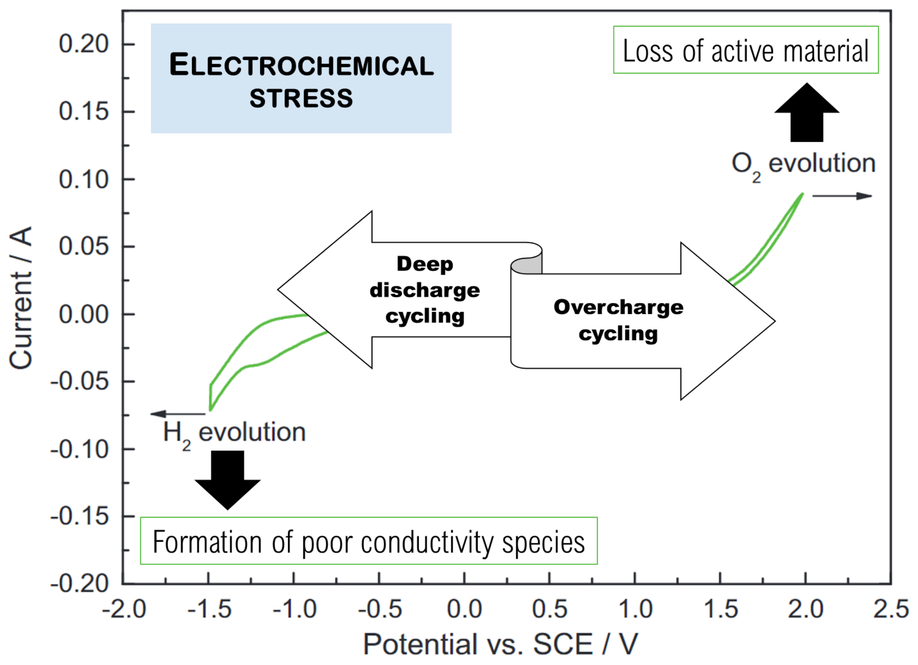

Figure 1: Current problem with manganese-based electrodes upon electrochemical stress. Adapted from Zhao et al. in Electrochimica Acta 56 (2011) 3781-3784.

PROPOSED SOLUTION

Our solution for overcoming and upgrading MnO_2 materials is the development of self-healing active materials by incorporating on the electrode 'new' and 'fresh' MnO_2 material.

This material will thus combine a highly active MnO_2 active material, with an enhanced N, S-doped reduced graphene, coated with a stimuli-responsive polymeric shell, operating as a pH-sensitive **ON/OFF controlled system**. The pH-responsive shell is composed by either acidic or basic polymers or by both (Figure 2):

Mechanism of ON/OFF

Polymeric shells are closed or deswelled at neutral pH; Upon a change on the surrounding pH, shells are opened or swelled at pH < 5 or pH > 9. This occurs thanks to the repulsive interactions that are generated upon the ionization of polymeric chains.

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