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NEWSLETTER CeFEMA

EDITORIAL

João Seixas

The CeFEMA newsletter focuses on R&D activities of the Center with relevant international impact in research and engineering in Materials Science, Condensed Matter Physics and Strongly Interacting Systems. The contributions presented in this number represent two examples of major achievements of researchers of our team in key areas in these fields.

This newsletter comes to you in very uncertain times. The present COVID-19 emergency casts a shadow over all human activities and Science is no exception. However, more than ever, we need Science to help us look at what lays ahead and tackle the associated challenges. CeFEMA is committed to these challenges on several fronts, some more focused on practical applications in Materials Science and Soft Matter, some of a more fundamental nature. In this issue we will look more closely at new technological pathways. You will find a review on Lithium-ion batteries and the related research work of our electrochemistry group in major areas of development in energy storage. Also, we will report on a technological breakthrough in portable devices for Nuclear Magnetic Resonance.

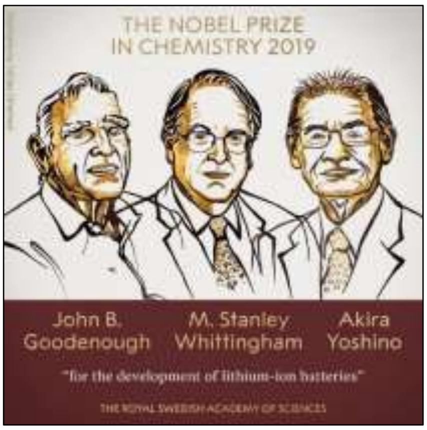
On April 1st we have restarted our regular seminar series where both graduate and undergraduate students will present their results in parallel with the usual research seminars by confirmed researchers. As the circumstances dictate, the seminars will be all presented remotely until we will be able to reconvene again in person.

We will also start a new series of Colloquia, the first one being given on April 7rd by Prof. Henrique Silveira (Mathematics Dep., IST) on epidemiological models, a key issue in our present situation. Seminars and outreach, which are open to the IST community and other institutions, are key activities of the Center, essential for both dissemination of knowledge and for the formation of our students. Let us therefore continue to make these occasions a special and lively moment in the life of CeFEMA. Stay tuned!

THE TRIUMPH OF LITHIUM-ION BATTERIES

The 2019 Nobel Prize in Chemistry

Membrane, chemical and electrochemical processes group (Electrochemical processes team)



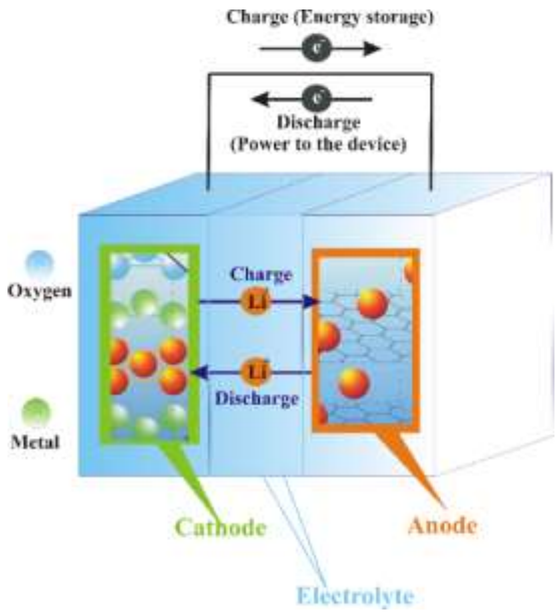
In October 9, 2019 it was announced that the 2019 Nobel Prize in Chemistry had been awarded to John Goodenough, Stanley Whittingham and Akira Yoshino "for the development of lithium-ion batteries." These three scientists received this distinction for their pioneering work in the early 70's in what has now become an indispensable power source in our everyday life. In fact, the development of Li-ion batteries (LIBs) led to a revolution in consumer electronics since the late 20th century. These devices are present in our cell phones, tablets and laptop computers, digital cameras, and more and more frequently, in the increasing market of electric vehicles (EVs). The market for LIBs was about 33 x 10^9 euros in 2018 and it is expected to increase to ca. 80 x 10^9 euros in 2024, mainly due to projected growth in the demand of EVs.

This expansion of the LIBs market could not have been possible without the contribution of this three 2019 Nobel Prize in Chemistry Nobel laureates. Stanley Whittingham was the first one to demonstrate that intercalation chemistry, namely the lithium insertion in titanium sulfide, could be put together with lithium metal anodes for

"STANLEY WHITTINGHAM WAS THE FIRST ONE TO DEMONSTRATE THAT INTERCALATION CHEMISTRY, NAMELY THE LITHIUM INSERTION IN TITANIUM SULFIDE, COULD BE PUT TOGETHER WITH LITHIUM METAL ANODES FOR APPLICATION IN BATTERIES. THEN, GOODENOUGH PROPOSED THE USE OF OTHER INTERCALATION COMPOUND, $LICOO_2$, ALLOWING THE REVERSIBLE INSERTION AND DE-INSERTION OF LITHIUM IONS AT HIGHER POTENTIALS, THUS INCREASING THE CELL VOLTAGE FROM 2.5 TO 4 V."

application in batteries. Then, Goodenough proposed the use of other intercalation compound, $LiCoO_2$, allowing the reversible insertion and de-insertion of lithium ions at higher potentials, thus increasing the cell voltage from 2.5 to 4 V. However, the use of Li metal anodes posed safety risks as, upon repeated cycling, the formation of deposits/dendrites could lead to short-circuits and, ultimately, to explosions. This dangerous drawback hindered the beginning of the commercialization of these devices. It was only in 1985 that Yoshino proposed the replacement of the Li metal by a much safer carbon anode, enabling the commercialization of the first LIB in 1991 by Sony. This cell had practical energy density of 200 Wh/L and specific energy of 80 Wh/kg. Today's commercial cells have tripled these values, with energy density of 650 Wh/L and specific energy of 250 Wh/kg.

Still, the high Li demand and the need to decrease the costs of these devices have lead researchers to look for new alternatives to the LIB, namely using magnesium and sodium-based systems. In fact, the electrochemistry group of CeFEMA had worked in a joint project with researchers from Belgrade University in the development of the sodium-ion battery [1]. The high abundance of sodium ion could dramatically decrease the costs of these new battery devices.



Taken from C.A.C. Sequeira et al. [1].

But the focus of CeFEMA's research in the field of electrochemical energy conversion and storage is not only based on batteries. Although Elon Musk likes to call them "fool cells", fuel cells are seeing tremendous advances in the last few years. It is natural that the CEO of Tesla sees them as threat to conventional LIB-based EVs. But fuel cell vehicles (FCVs) have undoubtedly several advantages over EVs, such as the fact that their fuel deposit can be quickly filled using the traditional supply system currently used for gas. CeFEMA researchers are studying lower-cost materials that can be applied in the fuel cell electrodes, thus allowing a significant decrease in the fuel cell cost and pushing forward the dissemination of FCVs.

Zoom meeting of the Electrochemical processes group.

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NUCLEAR MAGNETIC RESONANCE AT CEFEMA

Complex Fluids, NMR and Surfaces Group (NMR team)

Nuclear Magnetic Resonance (NMR) is a well-established experimental technique used extensively in materials science, industry and medicine. The noninvasive nature of the technique and its element selective characteristics make it a very powerful analytical tool of recognized importance. Its discovery by Isidore Rabi in 1936 and posterior major developments led to the attribution of several Noble prizes in Physics, Chemistry, and Medicine. At CeFEMA NMR has been used in materials science by the group of Complex Fluids NMR and Surfaces (CFNMRS) to study soft matter, addressing both the molecular dynamics and the molecular orientational order in the studied materials. A wide range of systems, including liquid crystals, liquid crystalline polymers, liquid crystalline dendrimers, polymer composites, ionic liquids and food materials have been investigated, using as probes mainly the NMR active elements hydrogen, deuterium and carbon-13.

Molecular dynamics studies are carried out based on the measurement of NMR relaxation times, particularly hydrogen spin lattice relaxation time T_1. When hydrogen T_1 frequency dispersions are obtained covering a wide range of frequencies, it becomes possible through relaxation models' simulations to identify and characterize the molecular motions in soft matter. This is achieved in CeFEMA's NMR laboratory thanks to the combination of standard and fast field cycling NMR techniques that cover the Larmor frequencies' range from 10kHz to 300MHz. While the upper end of this range (15MHz-300MHz) is spanned with constant field conventional relaxation measurements, the lower end (10kHz-9MHz) takes advantage of a home developed fast field cycling NMR relaxometer, unique in the world and patented in 2007 (PT 103705). An intense collaboration between the CFNMRS group and the IST Department of Electrical and Computer Engineering/INESC-ID allowed for this technological development and is about to deliver its 4th generation FFC NMR equipment at CeFEMA.

4th generation desktop NMR field cycling relaxometer developed at CeFEMA.

Orientational order studies in different anisotropic systems have also been carried out using both hydrogen and deuterium as active NMR elements. Resorting to the partially averaged dipolar and/or quadrupolar interactions, it was possible to establish a relation with elements of the ordering matrix allowing the determination of molecular order parameters which were used to characterize the systems studied.

The combination of orientational order and molecular dynamics studies in the same system affords a comprehensive analysis that brings to light hidden features particularly in composite systems where more than one population of active NMR elements may be present.

The research activity of the CFNMRS group over the last 5 years on molecular order and dynamics in soft matter by NMR techniques led to the publication of one book entitled "NMR of Liquid Crystal Dendrimers" [1], one book chapter entitled "Field-cycling NMR Relaxometry: Instrumentation. Model Theories and Applications" [2], 21 research articles, the completion of 4 MSc thesis and contributing to 2 PhD thesis.

> "THE COMBINATION OF ORIENTATIONAL ORDER AND MOLECULAR DYNAMICS STUDIES IN THE SAME SYSTEM AFFORDS A COMPREHENSIVE ANALYSIS THAT BRINGS TO LIGHT HIDDEN FEATURES PARTICULARLY IN COMPOSITE SYSTEMS WHERE MORE THAN ONE POPULATION OF ACTIVE NMR ELEMENTS MAY BE PRESENT."

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NEWS AND EVENTS

Upcoming seminars' cycle by LASYP staff (dates to be announced)

The topics

1. Solidification: general aspects

2. Homogeneous and heterogeneous nucleation. Nucleation and epitaxial growth in LPD (Laser Powder Deposition).

3. Structure of the solid / liquid interface. Interface structure and solidification entropy. Atomic mechanisms of growth of solids limited by crystallographic and non-crystallographic interfaces. Influence on the solidification microstructure.

4. Chemical segregation in solidification at equilibrium conditions at the interface. Scheil equation. Partition coefficient. Solidification out of balance.

5. Formation of the solidification structure in LPD.

6. Cellular and dendritic growth. Characteristics of dendritic structures. Response function of the dendritic interface. Competition in dendritic solidification. Solidification texture. Morphology of the LPD microstructures.

7. Equiaxial solidification. Transition between columnar and equiaxial growth in LPD.

8. Peritectic solidification. Competition between phases. Huziger model.

9. Eutectic solidification. Types of eutectic. Growth zone coupled in eutectic diagrams. Microstructure of eutectic alloys in LPD.The research activity of the CFNMRS group over the last 5 years on molecular order and dynamics in eutectic diagrams. Microstructure of eutectic alloys in LPD.

Regular Seminars' program

Weekly seminars alternating between students and established researchers.

Regular Colloquia program

Monthly Colloquia by outstanding researchers starting this Tuesday, April 7th (2020) at 15:00.

"Epidemiological models using ODE's: the COVID-19 case"

Henrique Silveira de Oliveira (Math Dep. IST)

Abstract: We present an overview of epidemic models given by ordinary differential equations. This is an introduction to a general audience. We apply these models to the present nCOVID-19 crisis.

Zoom meeting link: https://zoom.us/j/699415029

Zoom meeting ID: 699 415 029

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