

2ND INTERNATIONAL CONFERENCE ON

# IONIZATION PRINCIPLES IN ORGANIC AND INORGANIC MASS SPECTROMETRY



**Abstracts**

**MENORCA, SPAIN**

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MASS SPECTROMETRY IS, ARGUABLY THE MOST IMPORTANT ANALYTICAL SPECTROMETRIC TOOL OF MODERN TIMES AND THE ORGANIC AND INORGANIC MASS SPECTROMETRY COMMUNITIES ARE PROBABLY THE LARGEST GROUP OF SCIENTISTS WORKING AROUND A SINGLE TOOL. FOR BOTH COMMUNITIES MASS SPECTROMETRY CONCERNS ION CHEMISTRY AND PHYSICS WITH AN EMPHASIS ON SCIENTIFIC INSTRUMENTATION FOR MASS SEPARATION.

THIS CONFERENCE IS MEANT TO PROVIDE AN INTERNATIONAL FORUM BY WHICH ORGANIC AND INORGANIC MASS SPECTROMETRY RESEARCHERS AND USERS HAVE THE OPPORTUNITY TO SHARE THEIR KNOWLEDGE AND EXCHANGE IDEAS ON IONIZATION PRINCIPLES IN PARTICULAR.

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# Invited Lectures

## Invited Lecture I

### TRIBOELECTRIC NANOGENERATORS FOR SENSITIVE NANO-COULOMB MOLECULAR MASS SPECTROMETRY

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Ion sources for molecular mass spectrometry (MS) are usually driven by direct current (DC) power supplies with no user control on the generated charges. Such control over ion generation would bring a new parameter for MS, as well as new capabilities for experimental design. Here, we present the first rational approach to quantitatively control the number of ions generated for MS analysis using triboelectric nanogenerators (TENGs). Quantized charge generation was achieved by using TENGs, which have fixed charge density. The voltage of this quantized charge is sufficient to induce nanoelectrospray ionization (nanoESI). For a given nanoESI emitter, accurately controlled ion pulses ranging from 1.0 to 5.5 nC were delivered, with an onset charge amount measured at 1.0 nC. The flexibility of generating single polarity or alternating polarity ion pulses was also demonstrated. Spray pulse duration control was demonstrated to be between 60 ms and 5.5 s. The effective voltage for the quantized charge delivered was adjusted as high as 9 kV. This super-high voltage electrospray did not cause observable corona discharge that would typically damage the nanospray tip. Instead, highly sensitive (~0.6 zeptomole) MS analysis with minimum sample consumption (18 pL pulse<sup>-1</sup>) was achieved. Experiments also showed that native protein conformation can be conserved with this approach. Patterned ion deposition onto both conductive and insulating surfaces was also demonstrated. With increasing charge supplied, plasma discharge ionization was also attained. This simple, safe, and effective TENG-driven ion generation approach opens the possibility of charge-resolved mass spectrometric analysis and ion utilization.

## Invited Lecture II

### **ANALYTICAL MICROPROBES: GETTING MORE OUT OF LESS**

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The arsenal of techniques capable of getting chemical information from reduced spatial domains has been a constant in the analytical instrumentation. Such evolution has run in parallel with the extraordinary advances in the field of microscopy that have produced a deep impact in our vision of the world and the relationship between functionality and molecular structure. It was obvious since our access to the microscopic world that even the most homogeneous structures were far from being considered as such when the zoom was on. Microbeam analysts are challenged daily by the sophisticated problems which arise with our high-tech world, and the shocking voracity of bioanalysis for any tool capable of a better understanding of our living systems.

Since the early days of modern spectrochemical analysis where the capabilities of arc/spark to perform chemical analysis localized over an area of several square millimeters, a long journey has been run. One of the main advances has been the happy marriage of such techniques with mass spectrometry to get the best of both worlds. Nowadays, lasers, electron guns, ion guns, discharge lamps, electrospray jets, metal capillaries and many other approaches are used to create ions from reduced sample areas that are further sorted and detected in a mass spectrometer. The applications are still growing and it is still difficult to see if there is a limit.

The talk will provide an overview of analytical microprobes focusing in those involving lasers and gas guns. Thus, laser-ionization mass spectrometry, secondary ion mass spectrometry or low-energy ion scattering will be commented and compared with some other. Selected applications will be shown trying to emphasize the strengths of the techniques, without forgetting the inherent weaknesses of each one.

## Invited Lecture III

### **SPATIALLY RESOLVED ANALYSIS OF SOLID SAMPLES USING PLASMA-BASED MASS SPECTROMETRY TECHNIQUES: GLOW DISCHARGE AND LASER ABLATION**

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Inorganic mass spectrometric techniques and methods for direct solid analysis are widely required to obtain valuable information about the spatial distribution of major and trace constituents and/or isotope ratios in a wide variety of solid samples. Glow discharge mass spectrometry (GD-MS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) offer some unique and complementary analytical advantages for the direct analysis of solids. In both cases, mass analysers provide multi-element capabilities with relatively simple spectra (most of the elements of the periodic table can be determined), isotopic information and low detection limits.

In pulsed GDs (PGDs) a dynamic plasma is produced and different temporal ionization regions can be found during the pulse period. An adequate combination of pulsed ion source with time of flight mass spectrometry (TOFMS) enables time-gated detection of formed ions along the GD pulse period; in this way, a proper selection of the integration time window providing the highest analyte signal with minimum spectral interference is feasible. The coupling of a PGD to TOFMS allows obtaining multi-elemental depth-profiles with high depth resolution, isotope ratio measurements, and the simultaneous production of elemental and molecular information in high-tech materials.

On the other hand, the quantitative analysis and distribution of essential, toxic, and therapeutic metals as well as metalloids in biological tissues is a key task in life sciences today. LA-ICP-MS is a promising sensitive multi-element technique for the spatially resolved determination of trace elements in biological materials. However, the development of reliable quantitative strategies for the analysis of heterogeneous samples is still a task under development.

In this presentation, fundamentals, instrumentation and representative examples of applications carried out by our Group with these two complementary mass spectrometric techniques will be presented: GD-MS for depth profiling analysis of thin films (depth resolution in the nanometer range) and LA-ICP-MS for high sensitive imaging analysis of biological tissues (lateral resolution in the micrometer range).

## Invited Lecture IV

### FORMATION OF ATOMIC, MOLECULAR, AND BIOMOLECULAR IONS FROM AN ATMOSPHERIC-PRESSURE PLASMA SOURCE

Jacob T. Shelley,<sup>1</sup> Andrew J. Schwartz,<sup>2</sup> Courtney L. Walton,<sup>1</sup> Garrett M. MacLean,<sup>1</sup> Judy Wu,<sup>1</sup> and Gary M. Hieftje<sup>3</sup>

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Atmospheric-pressure glow discharges (APGDs) that utilize a flowing liquid as one or both electrodes have received increased attention lately as alternative sources for atomic emission spectroscopy. Though initially developed as alternatives to the inductively coupled plasma (ICP), these compact, low-power plasmas have been used more recently as tools for atomic and molecular mass spectrometry. Liquid-electrode discharges are unique in that they have the ability to create a wide-range of energetic species useful for atomization and excitation as well as desorption/ionization. These plasmas produce highly energetic species (*e.g.*, ions, metastable neutrals, fast electrons, etc.), which can lead to high-energy physical or chemical processes to fragment and ionize molecules. Meanwhile, lower energy ionization reactions can also occur due to the abundance of collisional cooling that takes place at ambient pressures.

This presentation will focus on the analytical capabilities of a liquid-electrode plasma called the solution-cathode glow discharge (SCGD). The SCGD is an APGD sustained on the surface of a flowing solution with ambient air serving as the discharge gas. The plasma volatilizes a portion of the liquid, and any chemical compounds contained therein, leading to desorption/ionization. Ions produced by the SCGD were sampled into a high-resolution Orbitrap mass analyzer. It was found that SCGD-MS could be used for the detection of atomic, molecular, and biological species directly from solutions. Furthermore, it was found that molecular species could be tunably fragmented through adjustment of SCGD operating parameters. For instance, peptides were tunably fragmented at atmospheric pressure, which led to 100% sequence coverage for many of the peptides examined. The power of this sequencing approach is further realized through coupling SCGD-MS with ultra-high performance liquid chromatography (UPLC). For the determination of elemental species, SCGD-MS was found to offer detection limits in the sub-ppb range for the analytes examined. The exceptional stability of the SCGD as an ionization source will be demonstrated through the measurement of isotope ratios. In the case of uranium, isotope ratio precisions with SCGD-MS were found to be on par with or better than the gold-standard approaches of thermal-ionization mass spectrometry (TIMS) or multicollector ICP-MS.

## Invited Lecture V

### META-IONIZATION OF POLYPEPTIDE POLYCATIONS IN THE GAS PHASE BY >10 eV ELECTRONS

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Gas-phase polypeptide polycations are easily produced by electrospray ionization (ESI), but the charge state is limited by the size and structure of the polycation, as well as the buffer composition and ESI conditions. For informative MS/MS fragmentation, higher charge state is desirable. Meta-ionization of polypeptide polycations by >10 eV electrons is known since late 1990s [1-2], and it has been used to enhance MS/MS [3]. However, technical difficulties remain in achieving high efficiency of this process. Here we present new results obtained using novel set-up for efficient trapping of ions – the omnitrapp (Fasmatech, Athens, Greece), and discuss the pros and cons of the gas-phase metaionization of polypeptide polycations for their structure determination.

1. Budnik, B. A.; Zubarev, R. A. *MH<sup>2+</sup> ion production from protonated polypeptides by electron impact: observation and determination of ionization energies and a cross-section*, *Chem. Phys. Lett.* **2000**, *316*, 19-23.
2. Zubarev, R. A.; Budnik, B. A.; Nielsen, M. L. *Tandem Ionization Mass Spectrometry of Biomolecules*, *Eur. J. Mass Spectrom.* **2000**, *6*, 235-240.
3. Fung, E. Y. M.; Adams, C. A.; Zubarev, R. A. *Electron Ionization Dissociation of singly and multiply charged peptides*, *J. Am. Chem. Soc.* **2009**, *31*, 9977-9985.

# Oral Presentations



## Oral Presentation I

### SPATIALLY RESOLVED ELEMENTAL DEPOSITION ON AGED LITHIUM ION BATTERY GRAPHITE ELECTRODES BY MEANS OF LA-ICP-MS

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In a typical lithium ion battery (LIB) system, a certain degree of performance loss can be witnessed because of various componential failures. Hence, understanding the different aging processes of the cell components is a major factor for improving e.g. cycle life, capacity, rate capability and safety of a battery system. A commercially often-applied cell system with regard to the cell chemistries, graphite as anode material;  $\text{Li}_1[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}]\text{O}_2$  (NMC) as cathode material plus a mixture of organic carbonates as electrolyte, was investigated. The NMC is known to degrade (faster) as soon as the upper cut-off voltage (usually 4.2 V) is increased to higher values. During a charge process, the lithium ions are migrating from the cathode through the electrolyte and separator to the anode in order to intercalate into the layered graphite structure where a reduction takes place (energy storage). Increasing the upper cut-off voltage leads not only to a higher amount of released lithium but also to an unwanted degree of transition metal (TM) oxidation. After dissolution of the  $\text{Mn}^{\text{x+}}$ ,  $\text{Ni}^{\text{x+}}$  and  $\text{Co}^{\text{x+}}$  ions they are as well able to migrate to the anode where a reduction and subsequent deposition on the surface takes place. These unwanted events favor the degradation of both, the cathode (e.g. structural instability and/or loss of electrochemical active TMs) and the anode (e.g. pore clogging), and is therefore an important puzzle piece in order to understand the complex phenomenon of lithium ion battery aging.

Due to a lack of reliable methods for  $\mu\text{m}$ -scale determination of the elemental distribution in aged LIB electrodes, a method using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was developed. Whole graphite electrodes were qualitatively investigated by means of a 193 nm ArF Excimer Laser as sample introduction system using 113 line scans per sample in order to visualize the lithium and TM deposition patterns. The qualitatively and spatially resolved elemental investigations revealed information about the relationship between the applied upper cut-off voltage and the amount of deposited lithium and TMs on the anode surface. The higher the cut-off voltage, the more lithium and TMs can be found on the graphite electrode. Furthermore, a relation between the inhomogeneous TM deposition pattern and varying pressure conditions within the cell could be revealed by substituting coin by pouch bag cells. These cells allowed to alter the inside pressure on the cell stack from the outside due to the use of a flexible foil as enclosure.

## Oral Presentation II

### NEW QUANTIFICATION STRATEGIES FOR DEPTH PROFILE ANALYSIS VIA PULSED GLOW DISCHARGE - TIME OF FLIGHT MASS SPECTROMETRY

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Pulsed glow discharges (PGD) coupled to time-of-flight mass spectrometry (TOFMS) offers great potential for depth profile analysis of materials, as it allows high acquisition rates and good mass resolution, together with depth resolution in the nanometer range. Moreover, thanks to the low intrinsic matrix effects of glow discharges, it can be obtained not only qualitative (signals *versus* sputtering time) information but also quantitative results (concentration *versus* sample depth) [1]. Nevertheless, there is still a lack of analytical quantitative approaches to achieve this last aim, especially when dealing with PGD sources.

In this communication we will present new quantification strategies for quantitative depth profile of major and minor elements, taken advantage of the intrinsic characteristics of the PGDs. Also, sensitivity improvements obtained thanks to the possibility to blank major components with a quadrupole in front of the TOFMS will be discussed. Within this context, we have developed quantification procedures with PGD-TOFMS for two types of samples: (i) stainless steel substrates contaminated with low concentrations of inactive rare earth elements (REEs) to investigate the penetration of contaminants, and (ii) electrodeposited multilayers and compositionally modulated alloys consisting of Cu and Ni-Cu layers that need to be characterized in terms of layer thickness and composition.

PGDs are characterized by three different dynamic regions due to the temporal application of the applied power: prepeak (just at the beginning of the power application), plateau (during the application of the power) and afterglow (after the applied power is off). The afterglow region is the most sensitive one and, so, it is convenient for analysis of the minor components; however, major components could be saturated. Therefore, we have used the afterglow region to obtain the best sensitivity for the REEs. However, for major elements saturating the detector in the afterglow (such as Cu signal in the electrodeposited multilayers) we will propose two strategies: (i) using the afterglow region for all the sample components except for the major element (Cu) that was analyzed in the plateau, and (ii) using the afterglow region for all the components but instead of Cu measuring the ArCu signal.

[1] L. Lobo, B. Fernández, R. Pereiro, *J. Anal. At. Spectrom.*, 32 (2017) 920-930

## Oral Presentation III

### WHERE IS THE LITHIUM?

### QUANTITATIVE DETERMINATION OF THE LITHIUM DISTRIBUTION IN LITHIUM ION BATTERY CELLS BY INDUCTIVELY COUPLED PLASMA TECHNIQUES

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The fundamental components of lithium ion batteries (LIBs) are the polyolefin separator, a graphitic anode, a cathode consisting of lithium transition metal oxides and an electrolyte based on a 1 M solution of LiPF<sub>6</sub> in linear and cyclic organic carbonates. Layered transition metal oxides, like lithium nickel cobalt manganese oxide (NCM) or lithium nickel cobalt aluminum oxide (NCA) are the most established cathode materials. The cycle stability i.e. the lifetime of the battery is inhibited by aging effects. During cycling, a part of the lithium content can be irreversibly lost or active lithium cannot be available. Depending on the active material of the electrodes, it may be that the capacity loss at the cathode is so high that it outweighs the capacity loss at the anode and thus active lithium remains during discharge in the anode. Due to the kinetical inhibition, the cathode is not able to accept further active lithium even though it is available in the anode. So this lithium is unavailable for the charge/discharge reaction.[1] Furthermore, there may be slow lithium diffusion in the electrolyte, at low temperatures. This can lead to metallic lithium plating on the graphite anode surface and thus to further immobilized lithium which can lead to a short circuit of the battery.[2] Therefore, the quantification of the lithium distribution is very important to understand the material in its electrochemical behavior.

In this work, the changes of the lithium distribution in LIB cells during cycling were studied. Furthermore, the effect of temperature was determined for T-cells and pouch bag cells. This was of importance for the performance deterioration of LIB cells during cycling and aging. The overall quantification and localization of lithium in/at the electrodes and the quantification of lithium loss in the solid electrolyte interphase and cathode electrolyte interphase and in/at other cell components is performed by inductively coupled plasma - optical emission spectrometry (ICP-OES).[3]

Furthermore in this work, we developed a laser ablation (LA) - ICP-OES method for the detection of short circuits on LIB anodes. We studied the spatially resolved analysis of three different pouch bag anodes (pristine, cycled and short circuit anodes), to improve the homogeneity of the lithium distribution.

[1] J. Kasnatscheew, *et al.*, Physical Chemistry Chemical Physics, 2016, 18, 3956-3965.

[2] J. Vetter, *et al.*, Journal of Power Sources, 2005, 147, 269-281.

[3] B. Vortmann-Westhoven, *et al.*, Journal of Power Sources, 2017, 346, 63-70.

## **Oral Presentation IV**

### **DIRECT SPRAY IONIZATION FROM TISSUE WITH APPLICATION TO NEUROSURGERY**

Evgeny Nikolaev

## Oral Presentation V

### ANALYSIS OF ACTIVE MATERIAL DEGRADATION IN LITHIUM ION BATTERIES BY MEANS OF TIME-OF-FLIGHT SECONDARY MASS SPECTROMETRY

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Research and development in the field of lithium ion batteries (LIBs) is facing continuously increasing demands concerning an enhanced energy density, a long cycle life, and improved safety properties for a vast diversity of applications ranging from portable electronic device to electric vehicles. Since a LIB is a highly complex system in which numerous effects occur simultaneously during charge/discharge cycling, it is necessary to apply suitable analysis methods to understand the origin and progression of detrimental effects that deteriorate the electrochemical performance. Amongst others, the dissolution of transition metals from positive active materials like  $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$  ( $x+y+z=1$ , NCM) and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO) can cause severe degradation effects on the surface of the carbonaceous negative active material. Beyond that, the dissolution of copper from the negative current collector can in turn negatively affect the positive active material. Specifically the dimensions of the deposits in the two-digits nanometer-scale and the small amounts of dissolved/deposited species requires a sophisticated analysis method which is capable of detecting these species with a high lateral resolution and a high mass resolution. These extraordinary high demands exceed the limits of most commonly used surface analysis-methods like e.g. SEM/EDX or XPS.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a powerful chemical imaging technique which provides elemental as well as comprehensive molecular information. The combination of high-resolution primary ion beams with conventional high dose sputter beams also allows depth profiling and 3D chemical characterization of inorganic and organic samples. To overcome limitations concerning an unknown initial electrode surface tomography, a vertical crater wall can be prepared by a FIB milling process prior to analysis. This way, limitations due to an unknown initial surface tomography can be overcome due to a minimal roughening and redistribution of material on the crater wall. Moreover, the application of the delayed extraction mode allows a combination of both high lateral resolution ( $\approx 100$  nm) and high mass resolution ( $m/\Delta m > 5.000$ ) which is required to separate the species of interest (Co, Ni, Mn, etc.) from intense interfering Li containing compounds at the same nominal mass. Finally, the results obtained from TOF-SIMS analysis can be cross-checked with other analytical methods to unravel the origin of rarely noticeable small-scale degradation effects that can cause severe consecutive reactions that lead to strong fading of the electrochemical performance

## Oral Presentation VI

### ANALYSIS OF NANOMATERIALS USING CE-SPICP-MS WITH MICROSECOND DWELL TIMES

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In this presentation, recent developments in inductively coupled plasma quadrupole mass spectrometry (ICP-Q-MS) instrumentation for nanomaterials research will be reviewed and an approach for direct, fast, and high-throughput nanomaterial characterization on a single particle level will be presented.

In the first part of the presentation, the current state-of-the-art in single-particle (spICP-MS) for the detection and characterization of single nanoparticles (NP) will be reviewed. Also, a custom-built high-speed data acquisition unit with 5  $\mu$ s dwell times ( $\mu$ DAQ) specifically tailored to the needs of spICP-MS [1] and capillary electrophoresis coupled to spICP-MS will be presented. The  $\mu$ DAQ was built in-house and enables continuous acquisition of signals from discrete ion clouds in the ICP with microsecond time resolution and 100% duty cycle. Fully time-resolved temporal profiles of individual single droplet or particle events can be recorded. The performance of this approach compared to conventional ICP-MS operation and selected applications will be discussed. Using a time resolution much higher than the typical duration of a particle-related ion cloud, the probability of measurement artifacts due to particle coincidence could be significantly reduced and the occurrence of split-particle events in fact was almost eliminated. Fully time-resolved temporal profiles of transient signals originating from single gold nanoparticles as small as 10 nm are presented. The advantages and disadvantages of millisecond *versus* microsecond dwell times are critically discussed including measurement artifacts due to particle coincidence, split-particle events, and particle number concentration.

Also, it will be discussed how separation methods coupled to ICP-Q-MS can aid the detection of NPs in complex mixtures. Specifically, a method that we developed for nanoparticle separation, size characterization, speciation, and quantification of gold and silver nanoparticles using capillary electrophoresis (CE) and ICP-MS [2] will be discussed and our recent efforts to expand this approach also to CE-spICP-MS [3] and different surface modifications of NP [4] will be presented.

[1] I. Streng, C. Engelhard, *J. Anal. At. Spectrom.*, **2016**, 31, 135-144.

[2] B. Franze, I. Streng, C. Engelhard, *Anal. Chem.*, 2014, 86, 5713-5720.

[3] D. Mozhayeva, C. Engelhard, *Anal. Chem.*, 2017, 89, 7152-7159.

[4] D. Mozhayeva, C. Engelhard, *Anal. Chem.*, 2017, 89, 9767-9774.

## Oral Presentation VII

### CHARACTERIZATION OF PHOSPHAZENE ADDITIVES AND THEIR DECOMPOSITION PRODUCTS IN LITHIUM ION BATTERY ELECTROLYTES BY GC-ORBITRAP-MS WITH DIFFERENT IONIZATIONS

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Nowadays lithium ion batteries (LIBs) are generally applied in consumer electronics and electric vehicles.<sup>1</sup> A variety of commercially available LIBs are run with carbonate based electrolytes. Due to the fact that the carbonates are highly flammable the safety risks e. g. in case of an accident involving hybrid electric (HEV) or electric vehicles (EV) have to be taken into account. One approach to overcome this drawback is the addition of a flame retardant additive. Additives of this group e. g. reduce the reactivity of the electrolyte towards the electrodes or the vapor pressure of the whole electrolyte and thereby lead to a reduced flammability. However, the used compounds have to be electrochemically stable versus the potentials LIBs are able to reach. Additives based on phosphazene moieties have already proven to reduce the flammability of LIB electrolytes.<sup>2</sup> Furthermore, the phosphazene moiety shows good responses especially when using MS e. g. with electron impact (EI) ionization.

In this work, electrolytes with the addition of 2% (v/v) of different known as well as novel phosphazene based additives were investigated by GC-Orbitrap-MS. The focus was the identification of characteristic fragments for the different introduced phosphazenes using the high-energy collisional dissociation (HCD) cell with N<sub>2</sub>. Furthermore, the aged electrolytes were scanned for possible aging products of the additives. Therefore, chemical ionization (CI) with methane as CI gas was applied in additional experiments. Samples ionized by EI showed good responses for the M<sup>+</sup> ions of the phosphazene additives and the NCI measurements displayed an excellent signal for the phosphazene moiety of the originally applied additive and the degradation products which kept the moiety. Based on these measurements the aging behavior of the phosphazene additives was investigated and possible degradation mechanisms could be proposed.

<sup>1</sup> F. Schipper et al. *Russian Journal of Electrochemistry*, 2016, **52**, 1095-1121.

<sup>2</sup> K. Xu et al. *Journal of The Electrochemical Society*, 2002, **149**, A622-A626.

## Oral Presentation VIII

### NEGATIVE IONIZATION MODE IN FAPA-MS

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Plasma-based Ambient Desorption/Ionization (ADI) sources are versatile devices for Mass Spectrometry analyses since they are capable of providing rapid, cost-effective, sensible and accurate information of relatively complex samples. In general, such sources rely on the production of several reagent ions by the interaction of atmospheric constituents and ionic and excited species produced in the plasma. Both positive ( $[(\text{H}_2\text{O})_n\text{H}]^+$ ,  $\text{NO}^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{O}_2^+$  or  $\text{N}_2^+$ ) and negative ( $\text{OH}^-$ ,  $\text{O}_2^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  or  $\text{CO}_3^-$ ) reagent ions are efficiently produced, which allows the ionization of a broad range of compounds.

Although positive ionization mode is undoubtedly effective for the ionization of a wide variety of compounds, certain analytically relevant substances are not easily ionized (e.g. organohalogens or fatty acids). In these situations, the use of the negative ionization mode can be an effective strategy as it eases the ionization and adds a certain degree of selectivity, simply because not every molecule is capable of forming a stable anion.

Negative ionization have been used in several works as an efficient way of detecting various kinds of compounds by means of several ionization reactions (mainly electron attachment, proton abstraction and anion attachment) represented by the detection of different analyte anions. In this sense, negative ionization mode in plasma ADI sources presents more complexity compared to the positive mode, where mainly protonated molecules  $(\text{M}+\text{H})^+$  and secondarily molecular ions  $\text{M}^+$  are detected. For this reason, detailed studies on negative ionization mechanisms are needed.

In this work, the Flowing Atmospheric Pressure Afterglow (FAPA) ionization source is studied in terms of negative reagent ion formation at different discharge parameters. Additionally, the introduction of dopants ( $\text{O}_2$  and  $\text{N}_2\text{O}$ ) is essayed for the promotion of specific reagent ions. Finally, several compounds generated mass spectra with a FAPA-MS system are shown.



## Oral Presentation IX

### **SPECIATION OF ORGANO(FLUOROPHOSPHATES IN LITHIUM ION BATTERY ELECTROLYTES BY SILMUTANEOUS 2D ION CHROMATOGRAPHY WITH ELECTROSPRAY IONIZATION AND INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY**

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Lithium-ion batteries (LIBs) are the fundament of modern consumer electronics and portable devices. Furthermore, these energy storage systems are the most promising technology for electric and hybrid electric vehicles. However, the main drawback for a better customer acceptance of lithium ion batteries is their capacity loss due to aging and therefore the reduction of their operating lifetime. The lifetime is limited due to several aging mechanisms inside the cell and its components. Currently applied electrolytes for LIBs usually consist of LiPF<sub>6</sub> as conducting salt dissolved in a mixture of different linear and cyclic organic carbonates, e.g. ethyl carbonate (DEC) and ethylene carbonate (EC). Despite the chemical and thermal instability in organic carbonates towards the P-F bond, LiPF<sub>6</sub> is the most commercial applied conducting salt today. However, due to its instabilities, hexafluorophosphate undergoes the decomposition to the highly reactive PF<sub>5</sub>. As a consequence, numerous decomposition products are formed and are an ongoing subject of investigations with different methods. The variety of decomposition products ranges from HF, inorganic and organic phosphates (OPs), dicarboxylates, diols and alkyl fluorides.

Since several of the identified decomposition products contain a P-F bond in their structure, there is a structural resemblance to certain nerve agents. Therefore, investigation of LIB electrolyte decomposition products in terms of qualitative and quantitative information is not only important for the electrochemical life time, but as well for potentially toxicological aspects. So far, only few information about the toxicity and even fewer about quantitative data are available in literature.

In this work, we present our approach to obtain structural and quantitative information about the decomposition products, especially the potential toxic compounds, by combination of ion chromatography with inductively coupled plasma mass spectrometry and electrospray ionization mass spectrometry.

## Oral Presentation X

### AIRBORNE LASER SPARK IONIZATION

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A novel ionization scheme for ambient mass spectrometry is presented and discussed. Desorption and ionization are achieved by a quasi-continuous laser induced plasma (LIP) ignited in front of the atmospheric pressure interface of a time-of-flight mass spectrometer. This setup comprises the advantages of i) an ambient probe, ii) electro neutrality, iii) low power consumption, iv) a sufficient duty cycle, v) a ubiquitous plasma medium (air) and vi) high sensitivity caused by the high electron number densities.

The plasma properties and operating conditions are investigated to understand the processes that lead to the formation of molecular ions. Comprehensive studies include optical emission spectroscopy, shadowgraphic shockwave visualization and time-of-flight mass spectrometry investigations. The observed MS signal (including reagent-ion signal, as well as analyte spectra) closely resembles the ionization behavior of other electrically-driven plasma-based ionization sources, such as DBD, LTP or DART. Conversely that means that although LIPs are commonly known to have temperatures way above 10.000 K and thus efficiently atomize and ionize molecules, MS spectra were obtained that showed the formation of intact molecular ions.

For an insight into the LIP properties the optical emission of the LIP is examined and exhibits a pronounced degree of dissociation into atomic and ionic species, which reflects the higher temperature and electron density inside a LIP. Accordingly, rather elemental (ICP-type) than molecular spectra should be expected. However due to the absence of such ions, we conclude that the analyte does not enter the hot center of the plasma itself. Moreover, the initial, highly-excited plasma species react cascade-like to lower energetic species via reactive collision with the surrounding atmosphere, which can then subsequently ionize molecules of interest. The concept potentially involves charge transfer, proton transfer, electron impact and photoionization.

These assumptions are confirmed via the shadowgraphs of the expanding shockwave around the LIP. An effective spatial separation between the two regions is maintained by concentrically expanding pressure waves resulting in a strongly unidirectional diffusion. Additionally, the strictly outbound matter transport suggests a rarefaction inside the plasma region for each plasma event.

## Oral Presentation XI

### SPECIATION OF ORGANOPHOSPHORUS AGING PRODUCTS IN LITHIUM ION BATTERY ELECTROLYTES VIA DRY PLASMA GC-ICP-SF-MS

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The most important but as well the most delicate part of a state-of-the-art lithium ion battery is the electrolyte; especially safety issues have to be investigated in the rising times of the electromotive industry. The electrolyte therefore has to meet challenging requirements with regard to performance, cycling stability and safety. Lithium hexafluorophosphate (LiPF<sub>6</sub>) in combination with a mixture of different organic carbonates is the outcome of long-term research and prevalent in commercial applications. Since the exclusion of moisture is nearly impossible, hydrolysis reactions of the strongly hygroscopic conductive salt occur during operation of the battery leading to chain reactions of the electrolyte and, eventually, to failure of the system.

Not only hydrofluoric acid is one of the toxic by-products of this decomposition route but also organophosphorus compounds with structural similarity to chemical warfare agents like sarin or soman are formed.[1] Though only present in small amounts in laboratory scale cells, the quantity becomes significant with regard to electromotive upscaling of the battery system. Since no molecular standards for these highly toxic compounds are commercially available, quantification of phosphorus was performed using an inductively coupled plasma-sector field-mass spectrometer (ICP-SF-MS) after gas chromatographic (GC) separation of species. Two different plasma conditions were compared; wet (addition of aerosol to the GC flow) and dry plasma conditions were evaluated in different resolutions with respect to separate the signal of interest <sup>31</sup>P ( $m/z$  30.974) from its main polyatomic interferences <sup>15</sup>N<sup>16</sup>O ( $m/z$  30.995), <sup>14</sup>N<sup>16</sup>O<sup>1</sup>H ( $m/z$  31.006) and <sup>12</sup>C<sup>18</sup>O<sup>1</sup>H ( $m/z$  31.007). Finally, it could be shown that operation in low resolution mode using dry plasma conditions can be performed independently from the matrix with respect to polyatomic interferences; this operation mode can be beneficial to improve detection limits and limits of quantification.

[1] S. Silver, Journal of Industrial Hygiene and Toxicology, 30 (1948) 307.

## Oral Presentation XII

### **MICROWAVE-ASSISTED ELECTROSPRAY IONIZATION ( $\mu$ AESI)**

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Electrospray Ionization (ESI) is one of the most extensively used ionization techniques for mass spectrometry, capable of generating gas phase ions from a variety of small and large molecules direction from solution phase. During the ESI process, molecules are released from solution as charged ions from highly-charged droplets. These droplets are formed from by an electrostatic, liquid free-jet expansion (Taylor cone), and while ion formation is thought to involve aspects of coulombic repulsion/explosion, all hypothesized ionization mechanisms involve some degree of solvent evaporation. Therefore, it is common for ESI sources to implement heating interfaces or gas streams in order to promote desolvation. Recently, our laboratory has developed a novel method to study the effects of microwave heating and desolvation upon the ESI process. Microwaves, at a frequency of 2.45 GHz, are focused near the tip of an ESI emitter by means of a novel waveguide structure. The coaxial waveguide focuses microwave energy in a very small and controlled volume. When the microwave radiation is absorbed, it induces very rapid evaporation through dielectric heating, modifying the features of the Taylor cone and affecting processes such as droplet generation, ionization efficiency, jet stability, and ion fragmentation. Here, we examine microwave-assisted electrospray ionization ( $\mu$ AESI) as a means to explore the mechanisms of ion generation, searching for methods to expand the capabilities of ESI through alterations in the fragmentation mechanisms and ionization processes.

## Oral Presentation XIII

### **THE HEART OF ICP: INNOVATION IN PLASMA LOAD COIL TECHNOLOGIES FOR ICP-OES AND ICP-MS**

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Load coils are required in ICP based technologies to sustain the plasma. Gas or liquid cooled load coils have been dominating the market for decades. A significant shift occurred with the introduction of FlatPlate technology in the beginning of this decade for ICP-OES, followed by the introduction of the LumiCoil<sup>1</sup> for ICP-MS earlier this year. Both innovations are self-cooling and integrate associated advances in RF generator design. Here we present FlatPlate and LumiCoil features and discuss their advantages over conventional coils in elemental analysis.

<sup>1</sup> US9591737 patent

## Oral Presentation XIV

### HPLC-MS<sup>n</sup> INVESTIGATION OF LITHIUM ION BATTERY ELECTROLYTE-RELATED AGING PRODUCTS

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Today's state-of-the-art lithium ion battery (LIB) electrolyte represents a compromise to achieve several goals at once like high dielectric constant, low viscosity, good reductive and oxidative stability and low costs. On this account, most electrolytes consist of different formulations of linear and cyclic organic carbonates with the addition of lithium hexafluorophosphate (LiPF<sub>6</sub>) as conducting salt. One issue of this compromise is the degradation of LiPF<sub>6</sub> due to thermal and chemical instability of the P-F bond.<sup>[1]</sup>

Upon charge/discharge cycling the electrolyte decomposes, leading to an irreversible capacity loss. Therefore, it is necessary to investigate the degradation products of cycled battery cells to get a better insight in this so-called aging process. Another aspect is the formation of the solid electrolyte interphase (SEI) which is essential for the prevention of further electrolyte decomposition at the carbonaceous anode due to its properties of being electrically insulating but lithium ion permeable. The structural elucidation of the resulting decomposition products of the SEI-formation process will help to develop electrolyte additives to improve this protective layer.

Both the presence of traces of humidity and elevated temperatures in the cell, the LiPF<sub>6</sub> starts to decompose to the reactive intermediate PF<sub>5</sub>, leading to fluorinated and alkylated phosphates after a reaction cascade.<sup>[2]</sup> These organophosphates show structural similarities to pesticides and nerve agents like sarin which implies the need of toxicological investigation, especially for the upscaling of battery systems and the application in electric vehicles.<sup>[3]</sup> Furthermore, the organic carbonates tend to polymerize to higher oligomers with unknown effects on the lifetime of the battery.<sup>[4]</sup>

The High Performance Liquid Chromatography (HPLC) hyphenated with an Ion Trap-Time of Flight (IT-ToF) Mass Spectrometer (MS) is a promising tool for the structural investigation of these aging products. It combines sensitive, non-destructive electrospray ionization for small and polar analytes with MS<sup>n</sup> fragmentation and high mass accuracy over all fragmentations levels.

In this work, the formation of aging products in LIB electrolyte were studied with HPLC-IT-ToF. Furthermore, the influence between electrochemical and thermal aging of LIB were compared, as well as different electrolyte compositions were considered for the formation of aging products.

[1] K. Xu, *Chemical Reviews*, 2004, 104, 4303-4417.

[2] C. Campion, et al., *Journal of the Electrochemical Society*, 2005, 152(12), A2327-A2334.

[3] V. Kraft, et al., *RSC Advances*, 2016, 6, 8-17.

[4] C. Schultz, et al., *Analytical Chemistry*, 2016, 88, 11160-11168.

## Oral Presentation XV

### INVESTIGATION OF LITHIUM LOSSES IN LITHIUM ION BATTERY ELECTRODES BY MEANS OF PLASMA-BASED TECHNIQUES

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Since the lithium ion battery (LIB) was established in the early 90's, it has to face challenging demands for mobile and stationary applications, respectively. The negative electrodes of the state-of-the-art LIB are based on carbonaceous material delivering a decent capacity of 372 mAh g<sup>-1</sup>. Lithium transition metal oxides (LiMO<sub>2</sub>; M = Mn, Co, Ni) are used as positive electrodes supplying capacities in the range of 150 mAh g<sup>-1</sup> like ternary mixtures of nickel, cobalt and manganese (LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (NCM111)) which show different benefits and drawbacks. On the one hand, high thermal stability and higher capacities in the charged state as well as less toxicity compared to LCO and LNO. On the other hand, these materials suffer from fading capacities during continuous cycling which cause is still under debate.

One postulated degradation mechanism is assigned to the passivation layer on the carbonaceous negative electrode which is called the solid electrolyte interphase (SEI). It is mainly formed during the first cycles due to the high reductive potential affecting the electrolyte and consuming active lithium. Furthermore, the kinetic hindrance of lithium re-intercalation into the transition metal oxide positive electrode host structure is another debated mechanism. [1,2] In order to quantify the lithium loss in both positive and negative electrodes, plasma-based analytical methods are well suited for the investigation of it.

In this work, inductively coupled plasma-optical emission spectroscopy (ICP-OES) and glow discharge-sector field-mass spectrometry (GD-SF-MS) are used for bulk and depth-resolved quantification of aged LIBs, respectively.

Therefore, several layered transition metal oxide cathodes were cycled in a Li metal full-cell set-up and investigated based on their lithiation degree after charge/discharge cycling via ICP-OES bulk analysis.

Furthermore, the lithium content in cyclic aged carbonaceous negative electrodes was depth-resolved quantified using GD-SF-MS. Due to a lack of suitable certified reference standards, self-prepared matrix-matched standard electrodes for external calibration of the GD-SF-MS system were synthesized. In order to examine the effect of SEI growth on cyclic aged carbonaceous electrodes, <sup>6</sup>Li isotope-labeled cells were investigated to elucidate the origin of lithium loss in negative electrodes.

[1] J. Vetter, P. Novák, M.R. Wagner, C. Veit, K.-C. Möller, J.O. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, A. Hammouche, *J. Power Sources*, **147** (2005), 269-281.

[2] J. Kasnatscheew, M. Evertz, B. Streipert, R. Wagner, R. Klöpsch, B. Vortmann, H. Hahn, S. Nowak, M. Amereller, A. C. Gentshev, P. Lamp and M. Winter, *Phys. Chem. Chem. Phys.*, **18** (2016), 3956-3965.

# Flash Presentations



## Flash Presentation I

### INVESTIGATION OF ENVIRONMENTAL FRIENDLY BINDER MATERIALS FOR LI ION BATTERIES BY MEANS OF PYROLYSIS-GC/EI-MS

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When talking about energy storage technologies, the lithium ion battery is the most promising candidate. This is due to the fact, that lithium ion batteries provide a good energy and power density as well as a good long-term stability. For such a reason they are already in use for a wide range of portable electric devices and are frequently mentioned in the context of hybrid electric vehicles. However, manufacturing those batteries is still a big topic, since there is a need of eco-friendly and safer materials.

In this case the analysis of water-based binder materials, like carboxymethylcellulose (CMC) and styrene butadiene rubber (SBR), are in the focus of this work, especially because polyvinylidene fluoride (PVdF) is commercially still in use and requires toxic and expansive solvents like N-methyl-2-pyrrolidone (NMP) for preparation. The application of Pyrolysis and GC/EI-MS enables the thermally decomposition of polymers followed by ionization and mass spectrometric analysis of generated decomposition products.<sup>[1][2]</sup> On this way it is possible to characterize the binder material by fingerprint analysis or even to identify specific decomposition products.

## Flash Presentation II

### ANALYSIS OF TiO<sub>2</sub> PARTICLES IN CONSUMER PRODUCTS BY TRIPLE QUADRUPOLE-ICP-MS

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Titanium oxide nanoparticles (TiO<sub>2</sub>, NPs) are widely used in pigments, sunscreens, cosmetics and more recently, in biomaterials such as metallic implants and scaffolds. In food industry, TiO<sub>2</sub> can be found as the E171 additive in various food products, mainly for whitening and texture. Although most products are labelled as containing E171, usually no information is given about the quantity and other characteristics like size and size distribution. It was shown that after uptake by the gastrointestinal tract TiO<sub>2</sub> particles are translocated to various organs. Therefore, in order to estimate potential health risks, analytical methods are required to characterise incorporated particles.

Among available techniques, single particle ICP-MS (spICP-MS) has gained importance in the characterisation of nanomaterials. In the case of TiO<sub>2</sub> particles, molecular and isobaric interferences usually require the measurement of lower abundant isotopes (e.g. <sup>47</sup>Ti or <sup>49</sup>Ti) instead of <sup>48</sup>Ti with a natural abundance of 73.72%. This might result in lower detection sensitivity, therefore, strategies are sought to improve detection limits in terms of particle size.

In this work, the Thermo Fisher iCAP TQ ICP-MS based on triple quadrupole technique is evaluated for its applicability in spICP-MS of TiO<sub>2</sub> particles. The instrument allows working in several measurement modes, e.g. reaction modes with NH<sub>3</sub> or O<sub>2</sub>. While using the single quadrupole modes measurement of <sup>47</sup>Ti is required, the triple quadrupole modes allow the detection of the most abundant isotope, <sup>48</sup>Ti. Analytical figures of merit for the different measurement modes will be presented. It turned out that best results in terms of particle detection was achieved monitoring the product ion <sup>48</sup>Ti<sup>14</sup>N<sub>4</sub><sup>1</sup>H<sub>10</sub> in the TQ mode. The optimised conditions were finally applied to the analysis of several consumer products in order to characterise their TiO<sub>2</sub> particle content.

## Flash Presentation III

### THE USE OF SINGLE CELL (SC)-ICP-MS TO EVALUATE METAL INCORPORATION INTO YEAST AND HUMAN CANCER CELLS

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The quantitative measurement of the metal composition of a cell is of great importance as metals are essential constituents. They are present in metalloproteins, metalloenzymes and others being indispensable in cell physiology. In addition, metal-based anticancer chemotherapeutic agents such as cisplatin are being used nowadays for the treatment of different types of human cancer. In this vein, several attempts have been made to quantify metals in cells, but most of them rely on bulk studies correlating total concentrations with the number or mass of cells. However, it is well known that biological populations are heterogeneous, and thus, suitable analytical methods are required to obtain information on metal concentrations in individual cells.

In this work, we propose the use of triple-quadrupole ICP-MS detection in combination with a sample introduction system to achieve individual cell introduction with high efficiency. Analytical figures of merit are presented and the methodology is applied to the analysis of yeast and human cancer cells.

Cisplatin is one of the most commonly used chemotherapeutics in the treatment of several cancers. Its main limitation is the development of associated resistance to the drug that yields in a significant reduction of intracellular platinum concentration. Therefore, intracellular Pt concentration can be considered as a biomarker of cisplatin resistance. The developed analytical strategy of SC-ICP-MS was applied to the evaluation of the uptake of Pt-species in cisplatin resistant and sensitive cell lines of ovarian cancer (A2780 cis and A2780). The results revealed a significantly different uptake in the two cell lines.

Following the same analytical strategy, the work was extended to selenium enriched-yeast that are a common form of Se used to supplement the dietary intake of this essential trace element in humans. The optimization of the Se-incorporation during the yeast growth and the characterization of the final products in terms of the selenium chemical forms present is requested by regulatory agencies. With the use of SC-ICP-MS it was possible to distinguish among Se-species spiked into the yeast cells and truly selenized yeast.

## Flash Presentation IV

### DIRECT SOLID ANALYSIS OF CARBONACEOUS ELECTRODES USING $^6\text{Li}$ -ENRICHED NON-AQUEOUS ELECTROLYTES IN LITHIUM ION BATTERIES BY GD-SF-MS

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The growing demands for renewable energies and the urge of reducing the human ecological footprint increases the attention for lithium ion batteries (LIBs) for mobile and stationary use immensely. While being a technology originating from the 1970s<sup>[1]</sup>, the state-of-the-art LIB uses carbonaceous materials and lithium transition metal oxides ( $\text{LiMO}_2$ ;  $M = \text{Ni}_x, \text{Co}_y, \text{Mn}_z$  ( $x+y+z=1$ )) as the negative and positive electrodes, respectively.

One major drawback of this technique is the successive capacity loss during operation. The formation in the first cycle and the ongoing growth of the solid electrolyte interphase (SEI) is one reason for these losses. The SEI forms on the carbonaceous negative electrode due to surface reactions because of reductive potentials by decomposition of electrolyte and therefore consumption of active lithium that cannot be utilized for electrochemical processes. This creates an electronic insulating but ionic conducting layer.<sup>[2]</sup>

Therefore, glow discharge-sector field-mass spectrometry (GD-SF-MS) is used in this work to analyze different carbonaceous electrodes of LIBs, aged under charge/discharge conditions. In detail, a  $^6\text{Li}$ -enriched electrolyte was prepared to perform an isotope dilution analysis (IDA) with depth profiling. Due to this combination, changes in the isotope-ratio could be monitored throughout the profile of the electrodes. This should provide a better understanding of the mechanisms behind the SEI formation and whether the decomposed lithium originates only from the electrolyte or from the positive electrode, as well.

The cyclisation experiments were conducted at different charging rates and numbers of cycles to obtain a better overview how the SEI forms over time under various conditions.

[1] J. Besenhard, G. Eichinger, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1976**, 68, 1-18.

[2] J. Vetter, P. Novák, M. Wagner, C. Veit, K.-C. Möller, J. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, A. Hammouche, *Journal of Power Sources* **2005**, 147, 269-281.

## Flash Presentation V

### **STUDY OF THE USE OF BIOCOMPATIBLE NANOSTRUCTURES TO IMPROVE CISPLATIN TRANSPORT IN CELL MODELS: FERRITIN AS NANOCAGE**

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Cisplatin (CDDP) is a widely used antitumor drug that reacts with the DNA generating the so-called DNA adducts. These adducts stop the DNA replication and the RNA transcription taking the cell into apoptosis. However, there are several problems associated with the use of this drug including undesirable side-effects (nephrotoxicity) and the resistance that the cells acquire in some cases. Recent studies have revealed that resistance may have associated low drug uptake. Therefore, one way to overcome such resistance is to improve the entrance of the drug inside the cells. For this purpose, cisplatin encapsulation into nanostructures might be an option.

Ferritin is the main iron storage protein in the body. It consists in 24 subunits that form a spherical structure, with an internal diameter of 8-12 nm. Within this protein, iron is accumulated in its nanoparticulated form. The different subunits can be easily dissociated by changing the pH conditions, and then can be recombined coming back to the initial pH conditions. Taking advantage of this possibility, CDDP can be encapsulated in this “nanocage”, improving the drug uptake in the cancer cells and minimizing the undesirable side-effects.

The aim of this work was the encapsulation of cisplatin inside the ferritin cavity. Once achieved, a comparative study of the uptake between encapsulated and free CDDP (not encapsulated) in different cell models will be done using ICP-MS to monitor Pt inside the cells.