Mass Spectrometry for Electrochemists

Peter Hatton, Jim Melling & Chris Williams, Hiden Analytical

Electrochemistry is concerned with the range of oxidation-reduction (redox) reaction that cause electrons to transfer between the molecules of reactants. It is the study of the relationship between electricity and an identifiable chemical change, which was first observed in 1780. The chemical aspect of this relationship was largely ignored until Michael Faraday established the fundamental laws of electrolysis, laying the groundwork for modern voltaic technology. Yet the chemical aspect of many redox reactions remains ambiguous, particularly with respect to the specific interfacial behaviour between electrodes and electrolytes.

Mass spectrometry was first highlighted as an essential tool for electrochemical gas analysis by Bruckenstein and Gadde in 1971. They explored the use of a porous electrode for real-time determination of volatile electrode reaction products using an electron impact ioniser. This electrode contacted the electrolytic solution on one side and the high-vacuum chamber of a mass spectrometer on the other, facilitating the rapid identification of products generated in a typical electrochemical reaction. This in-situ dissolved gas and off-gas analysis at the electrode surface provided a much better understanding of the reactions that occur in a galvanic cell or half-cell structure. Differential electrochemical mass spectrometry (DEMS) is a sophisticated tool that was engineered to improve upon this pioneering method. This technique has been improved and now offer quantitative insights into cell chemistry by integrating a mass spectrometer with a nanoporous gas diffusion electrode, enabling the acquisition of mass ion currents proportional to the electrode's faradaic current. Hiden Analytical manufacture several different Mass Spectrometry systems specifically for measurement and investigation of a wide variety of these Electrochemical applications. Thereby being a powerful tool for the researchers to gain insight and expand knowledge.

This article includes a brief overview of how mass spectrometry works for electrochemical studies, and we describe the main applications where mass spectrometry is being used by electrochemists

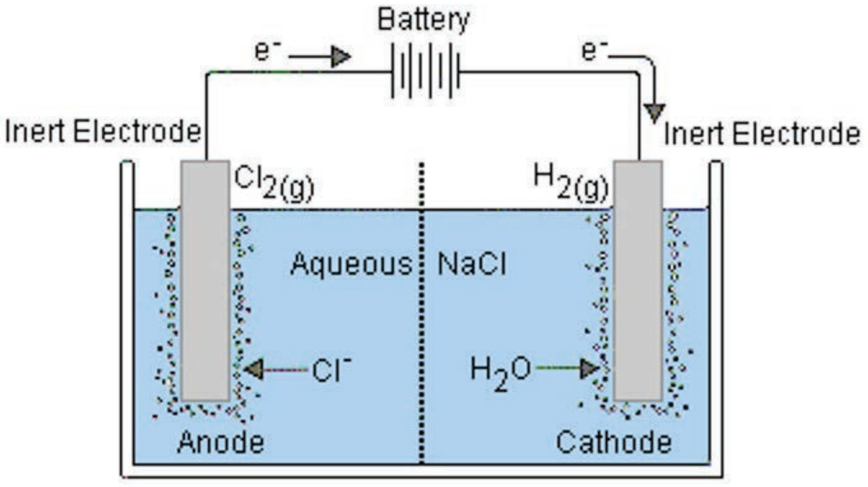


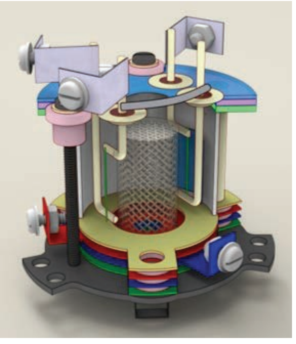
Figure 1: Inverted Electrochemical Cell (Electrolysis)

Differential Electrochemical Mass Spectrometry - How it works

Mass spectrometers separate ionised species as a function of their mass to charge ratio. The key to success for most mass spectrometry techniques is to present the species of interest as a gas or vapour at the optimum pressure for ionisation.

Operation depends on the conversion of gas molecules into charged particles, typically positive ions. This is achieved by electron bombardment from an electron beam generated from a hot filament wire. This process is known as electron impact ionisation. Ions are passed through the quadrupole mass filter and separated by mass /charge ratio before being detected by the detector, typically a Faraday cup and secondary electron multiplier dual detector.

The ion current detected is proportional to the partial pressure of the species measured.



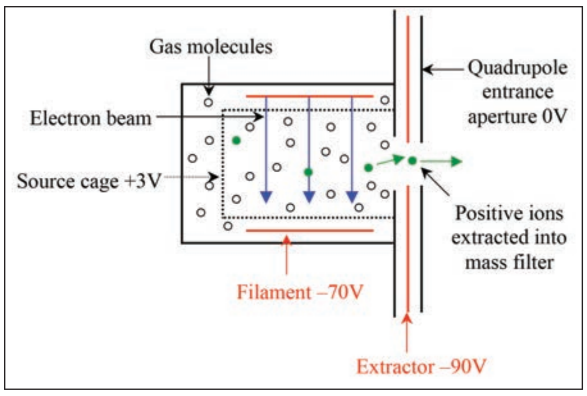


Figure 2: Electron Impact Ionisation.

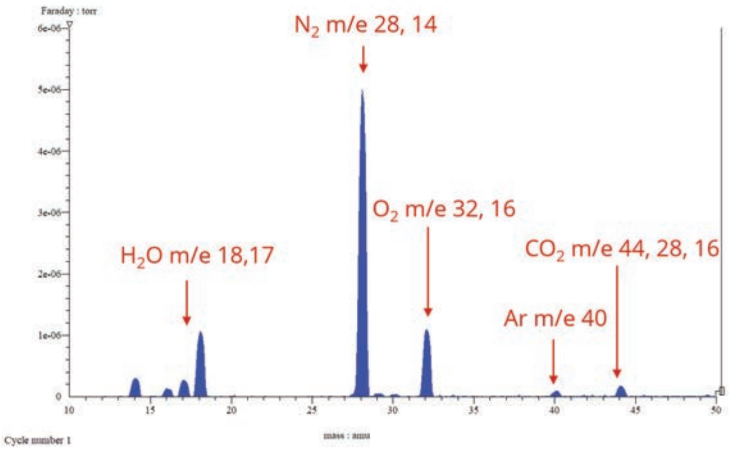
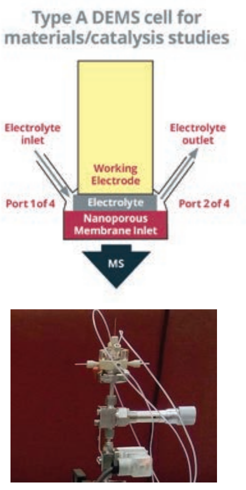


Figure 3: A typical mass spectrum showing species from air

The species of interest to electrochemists are dissolved within the electrolyte. The interface between the liquid electrolyte and the mass spectrometer in a 'DEMS' mass spectrometer is a nano porous membrane. The nano porous membrane allows the dissolved gas and vapour species generated in the electrolyte to permeate into the mass spectrometer ion source region, whilst maintaining a barrier to prevent the liquid entering.

High performance vacuum pumping maintains the high vacuum necessary for mass spectrometer operation.



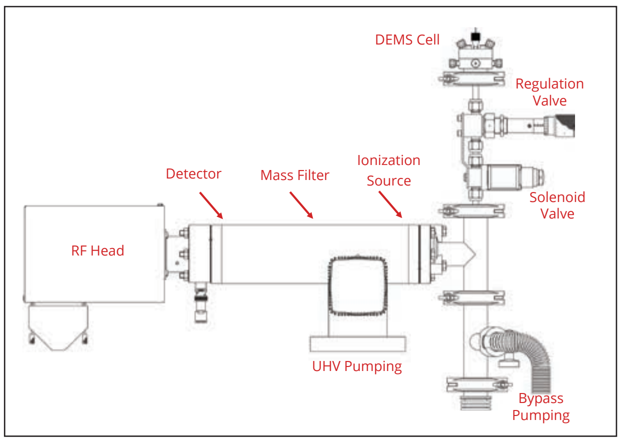


Figure 4: DEMS cell schematic and DEMS cell coupled to mass spectrometer

Figure 5: Probes can also be connected remotely to custom electrochemical cells

Figure 6: Bench top mass spectrometer configured for DEMS

OEMS - on-line electrochemical mass spectrometry:

In applications where a nano-porous membrane interface is not practical, off-gas from the electrolyte can be analysed by sampling through a capillary sampling tube. In off-gas experiments its critical to match the sample flow required by the capillary to the off-gas volume produced by the experiment. In some cases, this can be as low as 10 micro-litres per minute. Specialist sampling solutions for sampling at very low flow rates with good response time are offered as ultra-low flow capillary inlets that provide viscous flow sampling with fast response time.

Figure 7: Ultra low flow capillary inlet - 250 microlitres per minute

Applications of mass spectrometry for electrochemists

CO_2 Reduction

The technique of carbon dioxide, CO_2, reduction is used to produce fuels from CO_2. This is carbon capture from CO_2 that might otherwise go into the atmosphere and contribute to global warming. This technique of investigation derives from Redox reaction typical of an electrochemical half-cell. DEMS is an ideal technique for quantitative gas measurement due to the fast response, low detection limits and linearity, all in real time. Hiden instruments are noted for their stability and sensitivity. Scientists are looking to new materials such as graphene and carbon nanotubes to catalyse this reaction, leading to reduced energy requirements for the reaction and improved efficiency.

Co_2 Depletion

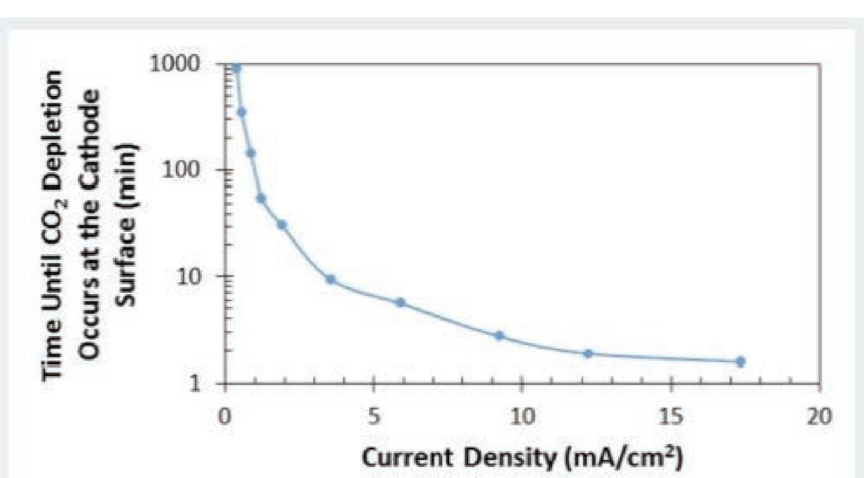
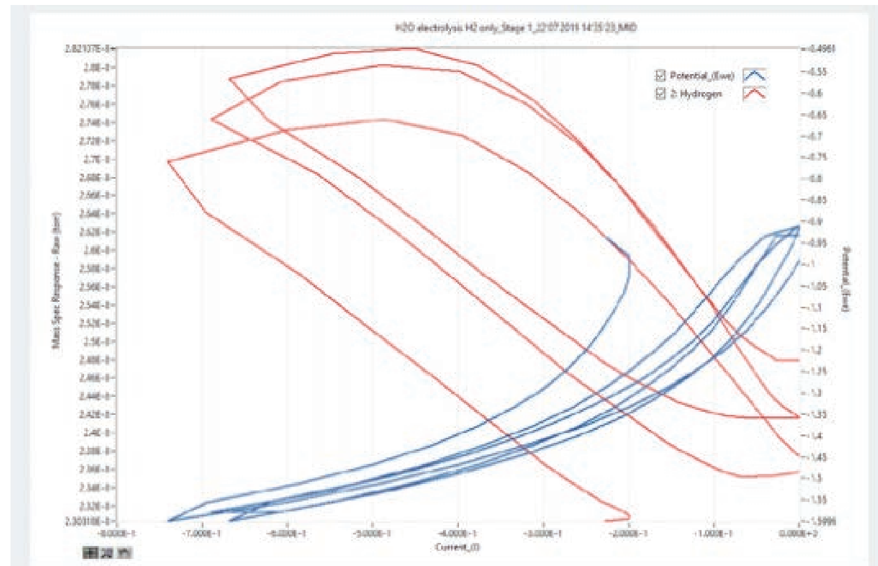


Figure showing Time before CO_2 depletion occurs at the surface of a polycrystalline copper foil cathode as a function of the applied current density in a static aqueous electrolyte.

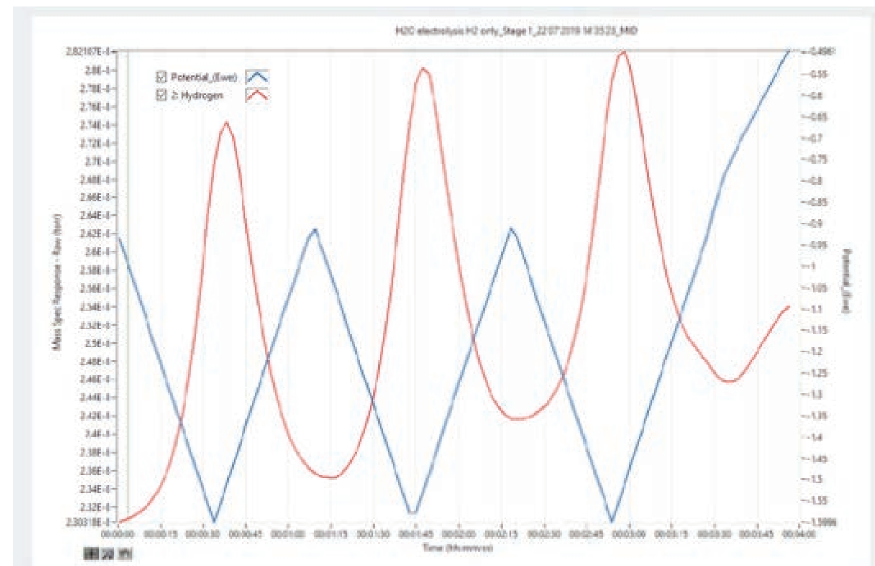
Water Splitting - Electrolysis

The technique of electrolysis uses electric current to drive a chemical reaction. A common method uses water electrolysis to produce hydrogen and oxygen. This is being investigated as a way of delivering small amounts of hydrogen for Fuel cells, either static or vehicular.

The graph below shows data for hydrogen (with other gases not shown for clarity). The changes in hydrogen evolution relate to the efficiency of the electrolysis. Hydrogen response and Potential is plotted versus Current and Time below.



Plot data of Hydrogen response and Potential versus Current.



Plot data of Hydrogen response and Potential versus time.

Hydrogen is typically generated by atmospheric condensation which is carried out at a large plant for better efficiency. However, this transfers the production cost to distribution. Transporting by road vehicle is inefficient and costly as the containers need to be highly pressurised and therefore thick walled and heavy. Pumping hydrogen is also less efficient as it is an extremely light gas, reducing the effectiveness of pumps to move along pipelines. Distribution of sufficient quantities for practical use becomes costly. Using hydrogen as a fuel has strong environmental benefits, as the waste product is water vapour. Other fuels such as methanol (also considered for fuel cell use) produce a mixture of gas products, water vapour and carbon dioxide (a greenhouse gas). An electrolysis station can produce hydrogen on-site for manufacturing plant use, or deliver directly using a refuelling station to a fuel cell vehicle. This localised distribution of hydrogen fuel thereby reduces safety concerns and transportation costs of hydrogen. Research into electrolysis aims to improve energy efficiency and so that this hydrogen production is economically viable, offers a key advantage over the current inefficient hydrogen transportation.

Electro Catalyst Studies

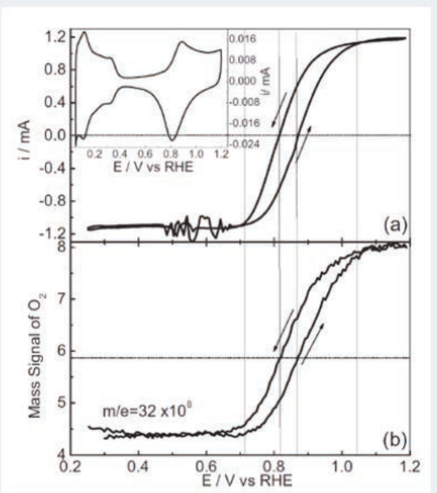
DEMS can be used to determine the kinetics of various oxidation and reduction reactions. Understanding these factors and reaction is of great importance to design and improve electrocatalysts. Also, to measure their efficiency and response to various different feedstock sources.

Mass spectrometer systems can simplify the analysis of otherwise complex cracking patterns from multi-component gas and vapour mixtures via the method of soft ionisation. This method provides user-defined ionisation to facilitate mass analysis and species discrimination with identification

Environmental Analysis & Electrochemistry

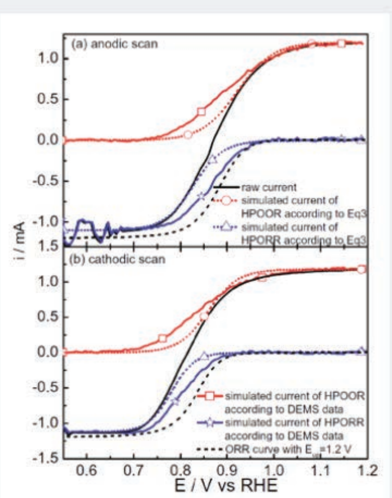
Potential and Hysteresis Behaviours

By following reaction intermediates and products, such as oxygen, O_2, hydrogen, H_2, and peroxides, H_2O_2, during cyclic voltammetry experiments, potential and hysteresis behaviours can be obtained.



Data from Electrochemistry Communications, 73 (2016) 38-41.

Cyclic voltammogram of (a) pc-Pt disk electrode in 0.1 M $HClO_4$ +2 mM H_2O_2 and (b) the corresponding potential-dependent mass signal of O_2. The inset shows the base CV of the Pt electrode in 0.1 M $HClO_4$ scan rate: 50 mV/s.



The raw i-E curve (solid line) at pc-Pt disk electrode in 0.1 M $HClO_4$ +2 mM H_2O_2, the simulated i-E curves for HPORR and HPOOR under the assumption that both reactions are mass-transfer limited (dotted line with triangle and circle), and the partial currents derived from the potential-dependent mass signal of O_2 (solid line with star and square). Then i-E curves for ORR (dashed line) at the same pc-Pt disk electrode recorded at 1600 rpm are also shown.

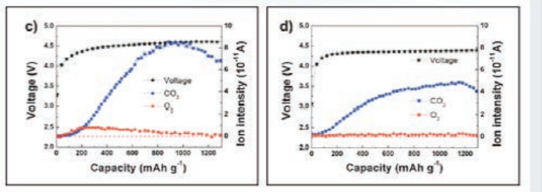
Lithium-Ion Battery Development

Lithium-ion batteries are being widely used due to their lightweight, rechargeable and power density. These technological advantages were recognised when three researchers shared a Nobel Prise for Chemistry, for key developments in Lithium-Ion Battery Technology. Active research and development continue to further improve power density, reduce recharge degradation and control temperature (which can degrade performance). https://news.uic.edu/researchers-prove-surprising-chemistry-inside-a-potential-breakthrough-battery

A significant proportional of the lithium-ion batteries manufactured goes to the automotive sector. Electric and hybrid vehicles are helping to reduce global emissions, whilst still maintaining the transport infrastructure.

GAS EVOLUTION RESULTS

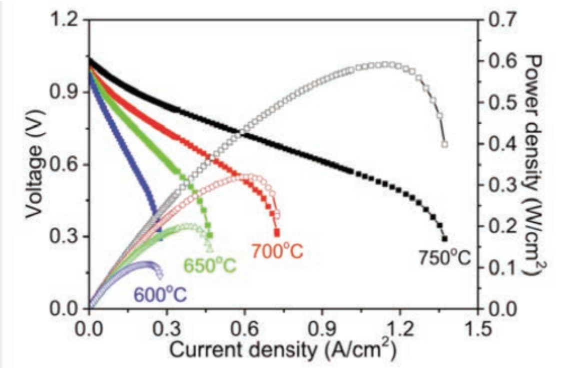
Due to the air sensitive and reactive nature of Lithium, typically a metal electrochemical cell is connected in-line with the Hiden mass spectrometer system. Hiden also can provide customised glovebox interfaces so that gas analysis can be carried out with the air-free environment of the glovebox with the gas analyser outside.



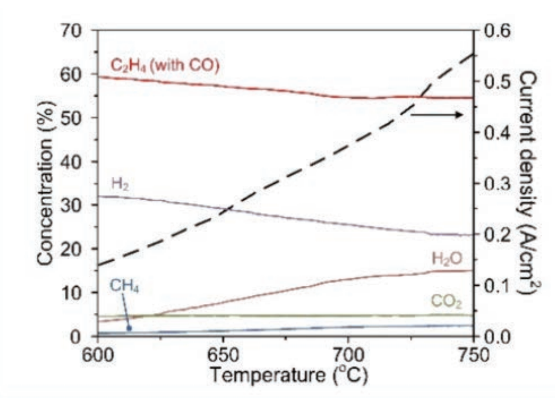
Gas evolution results of Li-O_2 cells c) without a catalyst and d) with a catalyst while charging as measured by DEMS.

Fuel Cell Studies

Solid Oxide Fuel Cells operate at high temperature. To improve efficiency, catalytic compounds can be used to reduce operating temperature and improve safety aspects. The Hiden mass spectrometer can be used to follow gas compositions for reaction dynamics and can read in thermocouple temperatures to incorporate into the data display. This research was carried out by Georgia Tech, using the HPR-20 to look at the effect of temperature on reforming of iso-octane as a fuel source, as there is already an infrastructure for distribution.



Typical performance of the fuel cell measured at 600 to 750 °C using iso-octane as fuel

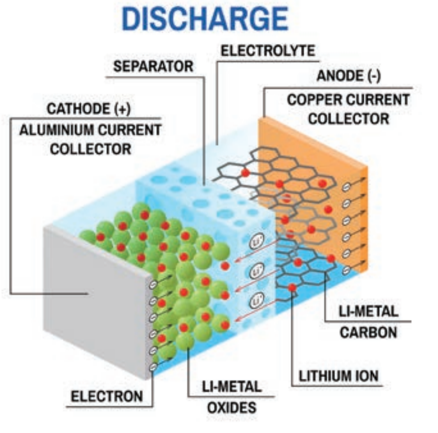


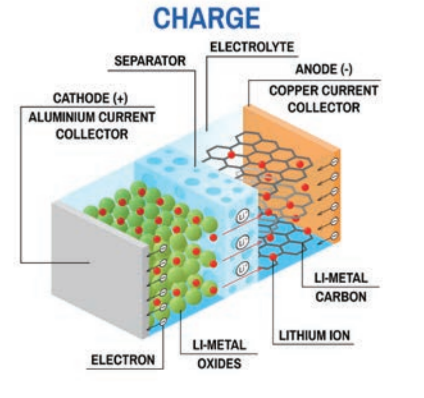
Effect of temperature on internal reforming of iso-octane. Concentration profile (as determined by the Hiden mass spectrometer of the effluent gas from the cell as a function of operating temperature.

Cathode Studies

The materials used for electrodes have a key effect on the performance of a battery. During battery usage, electrons should flow from the negative electrode (the anode) to the positive one (cathode) during discharge. For a rechargeable battery, they also need to flow in the reverse direction. Therefore, both the anode and cathode material properties influence the battery. The anode needs to readily lose electrons and cathode readily accept electrons. It was realised that Lithium being an element which readily loses electrons could be used for both electrodes to make a rechargeable battery.

Work done by the researchers Goodnough, Whittingham and Yoshino on electrode materials earned them the Nobel Prize for Chemistry in 2019. Their work on the development of Lithium Ions batteries showed that the effect of the electrode materials was critical to achieve safe and powerful batteries, enabling the many lightweight portable electronic devices in today's market. Initially Lithium metal was used, but it is reactive to air and could be explosive in the device. The Lithium element was replaced by Lithium ions, supported within a metal sulphide structure, so that the batteries were no longer explosive. By changing the sulphide material to a metal oxide, the capacity was doubled. The anode material was changed to carbon-based, which stored the lithium ions within the structure (intercalated), avoiding reactions with the electrode materials. This gives the battery a longer lifetime, due to the stability during the discharge and recharge cycle. These developments in materials greatly improved efficiency of a product that is so ubiquitous, especially for portable electronics. However, further improvements in materials chemistry are possible and many researchers are looking at materials for the electrodes and electrolyte which transport the ions and electrons, which can deliver higher capacity, more stable hysteresis during discharging and recharging cycles.





Conclusion

Mass Spectrometry provides an insight into electrochemical reactions not available by other techniques. The specificity, dynamic range and speed of response provided by mass spectrometry opens a window of discovery into the current/voltage dynamics of the electro-chemical world.

As the world moves to use more battery and hydrogen power in the future, the research from the applications discussed above will help provide efficient, reliable and affordable solutions.

New e-book Provides Water and Wastewater Analysis Solutions

Analytik Jena has published a new e-book for water and wastewater analysis. It demonstrates efficient methods and solutions for a wide range of selected routine and special applications. The e-book focuses on some central areas of water and wastewater analysis: In addition to the analysis of TOC/TNb and AOX, elemental analysis, and UV/Vis spectroscopy, the e-book also highlights molecular biological detection solutions.

"Water and wastewater analysis is a crucial component of the actions taken by municipalities and states to continuously improve water recycling processes and to make available water resources safer. It is a key element of environmental monitoring," said Bernd Bletzinger, team leader of Analytik Jena's environment industry team. "Our mission is to support customers worldwide with instruments and solutions to improve their services and processes and, thus, sustainably increase the quality of environment and life. This e-book was created by us following this intention."

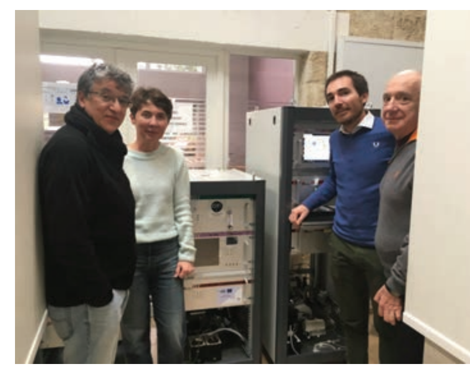
The new e-book highlights both methodological and technological ways to meet the current challenges in water and wastewater analysis. Today, the entire field of environmental analysis is facing steadily increasing numbers of samples, challenging sample matrices as well as dwindling financial and human resources. Analytik Jena particularly addresses these demands with the application examples and solutions demonstrated in the e-book and therewith provides its expertise to all laboratories in the environmental sector.

The e-book 'Water and Wastewater Analysis' marks the start of Analytik Jena's new environmental campaign, which bundles the Company's many years of experience and expertise in environmental analysis.

More information online: ilmt.co/PL/MZGa

For More Info, email: 54877pr@reply-direct.com

Collaboration to Measure Atmospheric Pollution Announced



Chromatotec recently welcomed a research team from the PRAT (Atmospheric Reactivity Platform) to its laboratories after partnering with them on air pollution control and measurement solutions. Managed by the CNRS and University of Orleans, the PRAT studies the impact of gaseous and particulate pollutants emitted by human activity (transport, pesticides, heating, industrial activities) on health, climate and the environment. Chromatotec collaborates with the ICARE-CNRS Laboratory through analytical development of GC-MS techniques for atmospheric measurement of volatile and semi-volatile organic compounds. The two entities will combine their expertise to validate the analytical system performance.

More information online: ilmt.co/PL/0dL9

For More Info, email: 55096pr@reply-direct.com

ADVERTORIAL

New Multi-Parameter Monitor/Controller for Water Treatment Applications Demanding High-level Performance

Myron L® Company's new 900 Series Multi-Parameter Monitor/Controller combines accuracy, reliability, simplicity, and flexibility. It's the ideal instrument for even the most demanding water treatment applications.

Measurement capabilities include: Conductivity, Resistivity, TDS, Salinity, pH, ORP, Temperature, mV input, Flow/Pulse, a multi-parameter 4-20/0-20 mA input, and % rejection. Standard outputs include a 0-10 VDC recorder output, a relay output, and a remote alarm output. Optional outputs include 4-20/0-20 mA, RS-485, two additional Relays and one additional remote alarm.

The instrument's display can show up to 4 measurements simultaneously. Sensor setup allows the user to eliminate error due to cable length and enter custom cell constants for conductivity sensors. Its 3.5" touchscreen and intuitive GUI make it simple to setup, simple to use and simple to adapt to your specific needs.

The Myron L® Company 900: a high level performer for applications where high-level performance is an absolute requirement.

More information online: ilmt.co/PL/3doj

email: 55259pr@reply-direct.com