ELECTROCHEMISTRY APPLICATIONS

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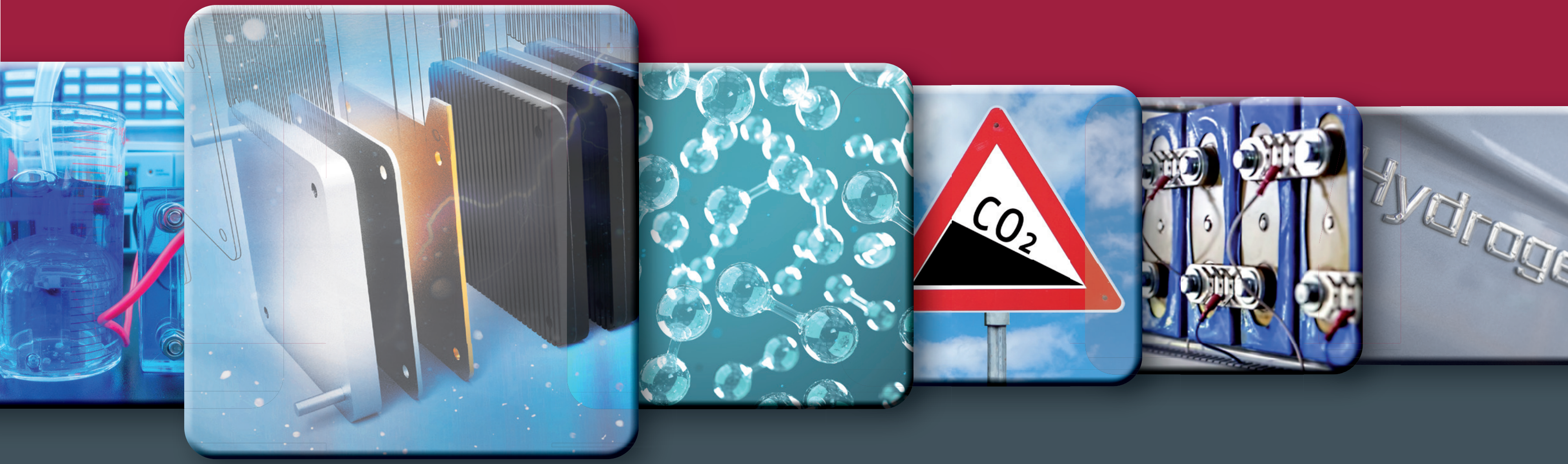


Electrochemistry Applications

INTRODUCTION

Electrochemistry Applications

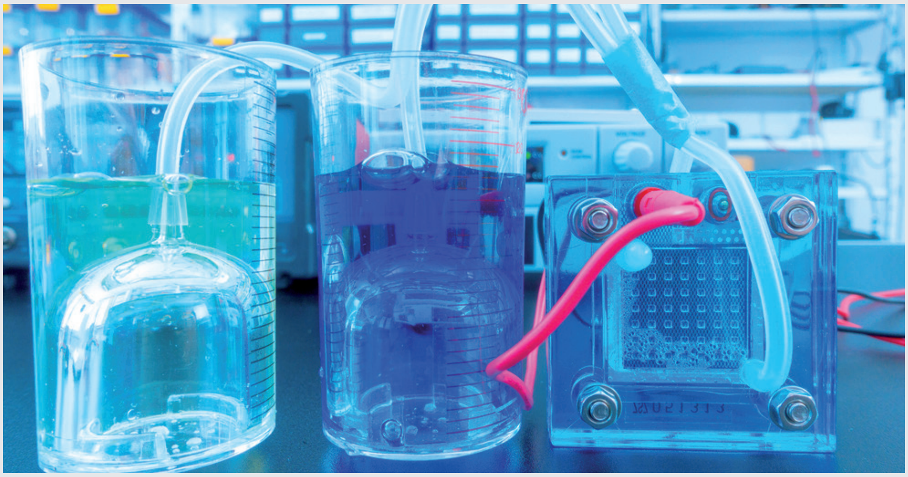
Electrochemistry is concerned with the range of oxidation-reduction (redox) reactions that cause electrons to transfer between the molecules of reactants. It is the study of the relationship between electricity and an identifiable chemical change, which was first observed in 1780.

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 ionizer. 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.

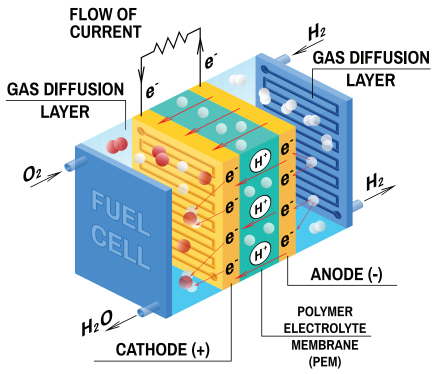
Hiden Analytical manufacture several different Mass Spectrometry systems specifically for measurement and investigation of a wide variety of these Electrochemical applications. Thereby being a powerful tool for the researchers to gain insight and expand knowledge.



Contents

RESEARCH TOPICS:

- Fuel Cells
- Electrolysis, Water Splitting, Hydrogen Storage
- Electrochemical Reactions
- Water Treatment



APPLICATIONS OF DEMS:

- Hydrogen Oxidation Reaction
- Oxygen Reduction Reaction
- CO_2 Reduction
- Methanol/Formic Acid Oxidation
- Ethanol Oxidation
- Ammonia/Hydrazine Oxidation
- Cathode Effects
- Battery Cycling
- Electrolyte Reactions in Batteries
- Other Fuel Cells (Borohydride, DMFC)
- Mechanistic Investigations on Methanol Oxidation
- Electrochemical Oxidation of Organics in (Waste-) Water Treatment
- Electrochemical Oxidation of CO

CO$_2$ Reduction

The technique of carbon dioxide, CO$_2$, reduction is for producing fuels from CO$_2$. This is carbon capture of 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, Differential Electrochemical Mass Spectrometry, 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

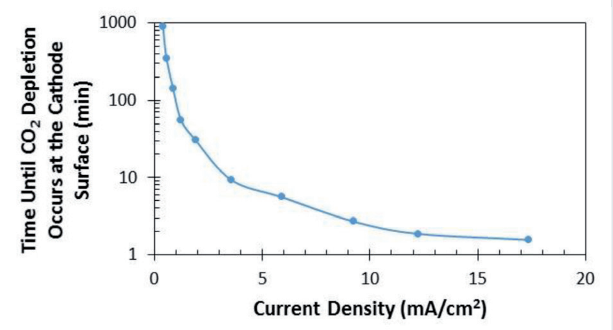
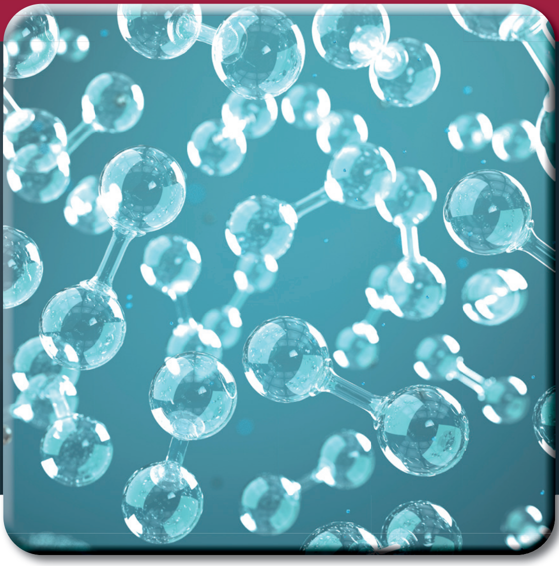


Figure showing Time before CO$_2$ depletion occurs at the surface of a polycrystalline copper foil cathode as a function of the applied current density in a static aqueous electrolyte.

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 smaller amounts of hydrogen for Fuel cells, either static or vehicular.

Cost to transport hydrogen is high. Hydrogen is typically generated by atmospheric condensation which is carried out at a large plant for better efficiency. However, this transfers the production cost on 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.

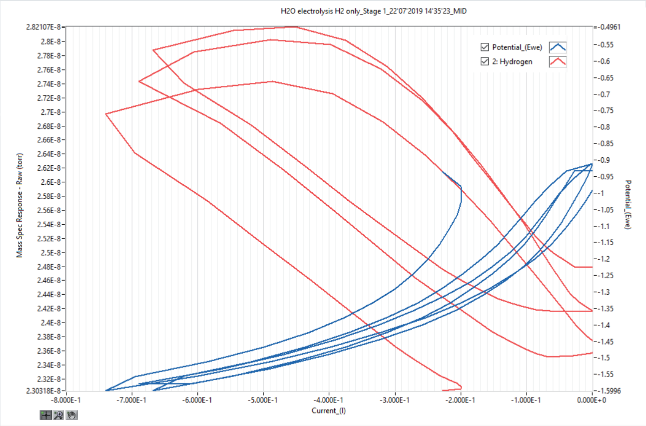
Using hydrogen as a fuel has strong environmental benefits, as the waste product is water vapour. Other fuels such as methanol (also considered for fuel cell use) produce a mixture of gas products, water vapour and carbon dioxide (a greenhouse gas).

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.

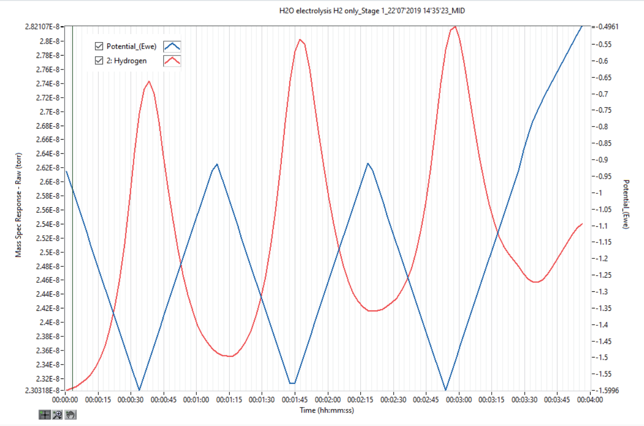
Research into electrolysis aims to improve energy efficiency and so that this hydrogen production is economically viable, a key advantage over the current inefficient hydrogen transportation.

EGASOFT

Hiden software, EGAsoft, allows plotting of the mass spectrometer response against electrical factors. 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.



Plot data of Hydrogen response and Potential versus Current.



Plot data of Hydrogen response and Potential versus time.

Electrocatalyst Studies

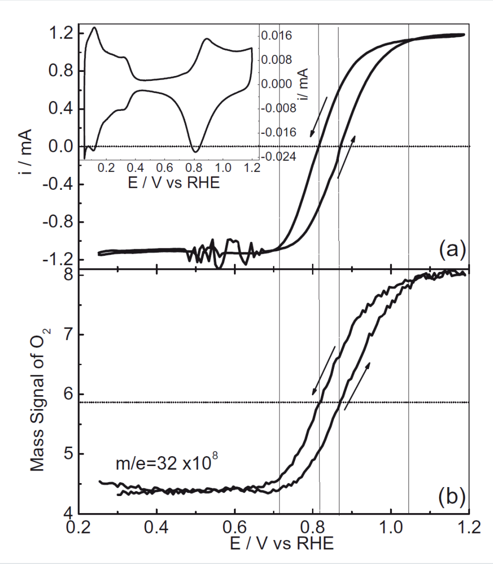
Catalysts allow a less energetic pathway for chemical reactions. Those used in Fuel Cells are vitally important, by lowering temperature of use and improved practical efficiency, However, these catalyst materials, while not consumed during the reaction, can have their efficiency reduced by impurities in feedstock.

DEMS, Differential Electrochemical Mass Spectrometry 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.

Hiden 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.

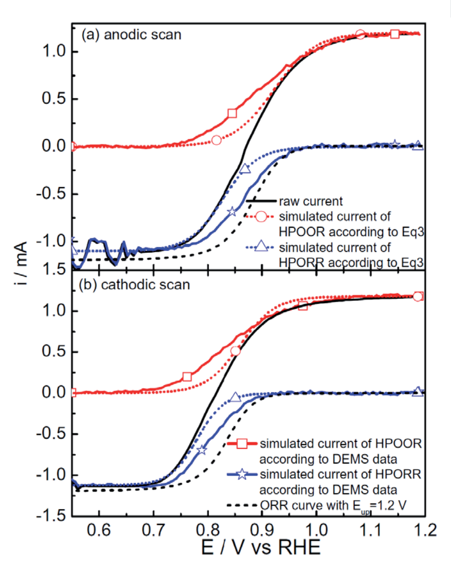
POTENTIAL AND HYSTERESIS BEHAVIOURS

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.

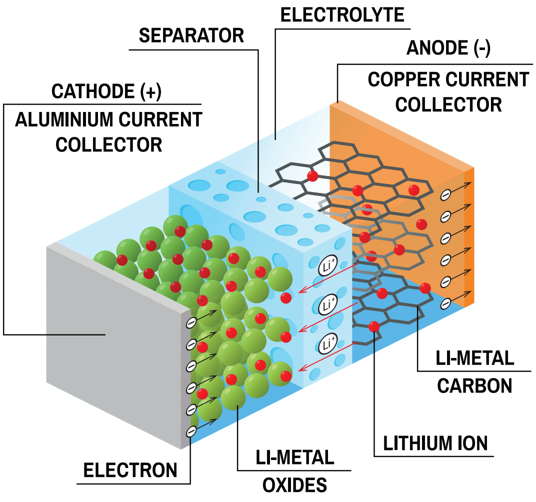
Lithium Ion Battery Development

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 Prize 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).

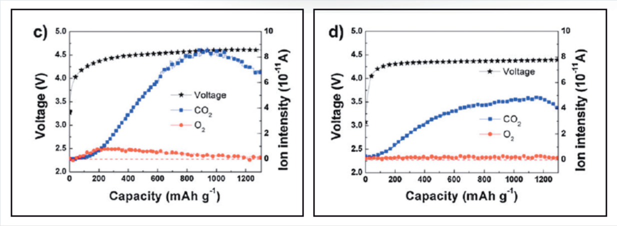
https://news.uic.edu/researchers-prove-surprising-chemistry-inside-a-potential-breakthrough-battery

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.

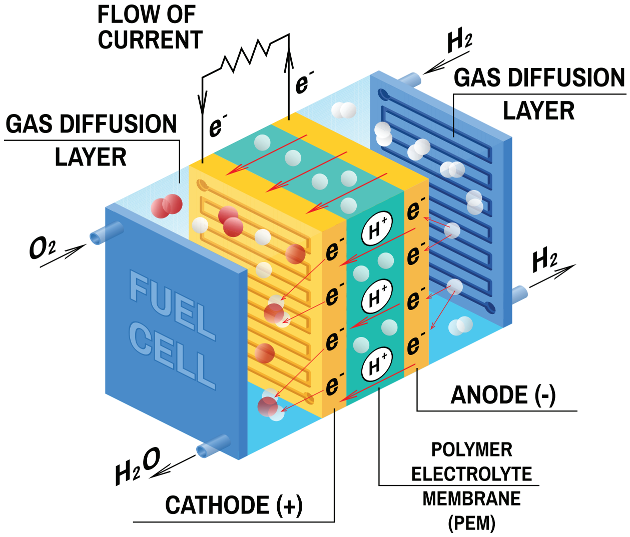


GAS EVOLUTION RESULTS

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.



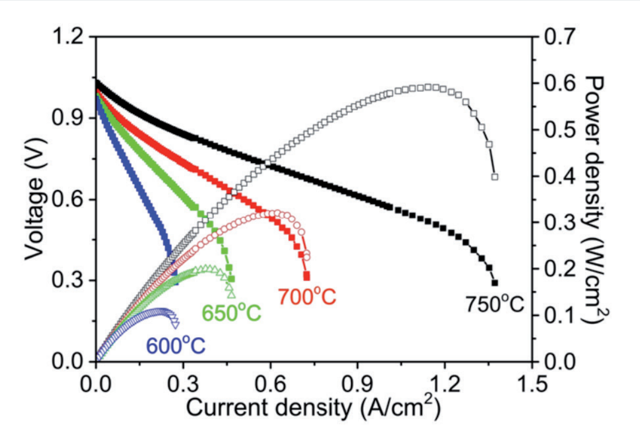
Fuel Cell Studies

Solid Oxide Fuel Cells operate at high temperature. To improve efficiency, catalytic compounds can be used to reduce operating temperature and improve safety aspects.

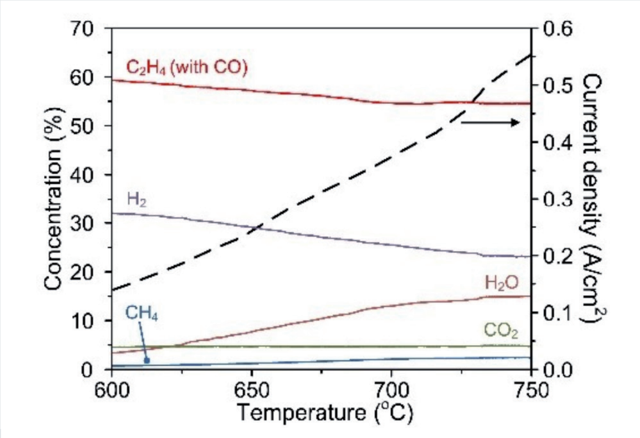
The Hiden mass spectrometer can be used to follow gas compositions for reaction dynamics, and also can read in thermocouple temperatures to incorporate into the data display.

This research was carried out by Georgia Tech, using the HPR-20. The performance of iso-octane as a fuel source, as there is already an infrastructure for distribution.

HIDEN MASS SPECTROMETER



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

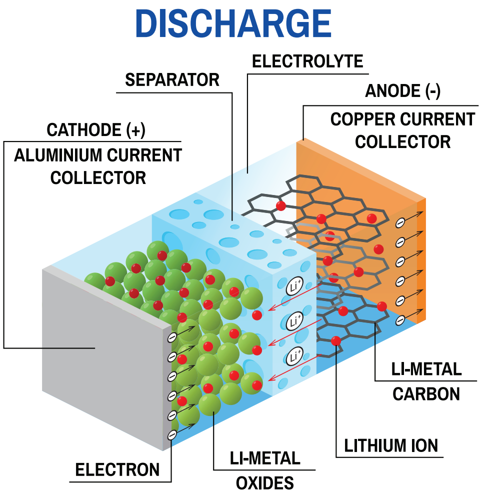
The materials used for electrodes have a key effect on the performance of a battery.

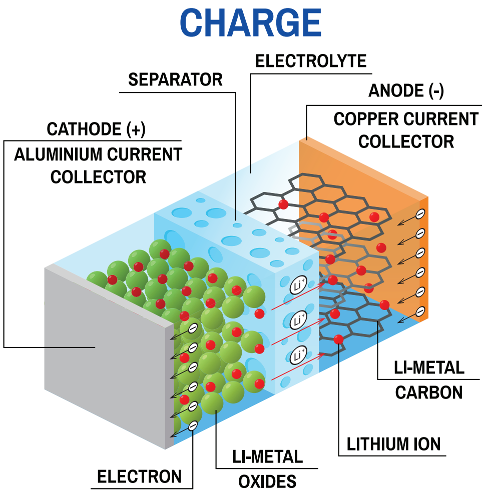
During battery usage, electrons should flow from the negative electrode (the anode) to the positive one (cathode) during discharge. For a rechargeable battery, they also need to flow in the reverse direction. Therefore both the anode and cathode material properties influence the battery. The anode needs 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 effect 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, but these were 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, making the battery have considerably longer lifetime. This is because the ions are stored within the structure (intercalated) rather than reacting with the electrode materials. This makes the battery longer lifetime, due to the stability during the discharge and recharge cycle.

These developments in materials greatly assisted the 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 transports the ions and electrons, which can deliver higher capacity, more stable hysteresis during discharging and recharging cycles.





The Hiden HPR-40 DEMS is a bench top or mobile cart mounted module for analysis of dissolved species in electrochemistry. The system is modular and adaptable. The system includes two differential electrochemical mass spectrometry **'DEMS'** cell inlets, designed for material/ catalysis studies, cell type A, and electrochemical reaction studies, cell type B.

For applications where **online electrochemical MS, OEMS**, from an existing cell or reactor is required, a range of standard inlet options is available offering both evolved off-gas and dissolved species analysis solutions.

Electrochemical cells that can be interfaced to the Hiden HPR-40 DEMS system include selected models from:

Redoxme AB, and EL-Cell®

The Hiden DEMS instrument is easy to setup and the electrodes and electrolytes can be easily changed, either for the supplied DEMS cells, or the researchers own DEMS cells. Hiden supply EGAsoft, an application specific software which can measure the gas products and allows plotting the mass spectrometer response against electrical factors, for example the hysteresis of the current potential vs SHE (standard hydrogen electrode). This is extremely useful when surveying various combinations of electrode and electrolyte as the data is gained in real time.

Furthermore Hiden SIMS instrumentation can assist with materials characterisation, providing elemental and molecular, surface and through thickness analysis. See Hiden SIMS Applications brochure, TDS 202, for more details.


SIMS APPLICATIONS

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SIMS Applications

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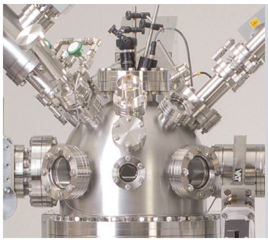
HidenAPPLICATIONS

Hiden's quadrupole mass spectrometer systems address a broad application range in:

GAS ANALYSIS

- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

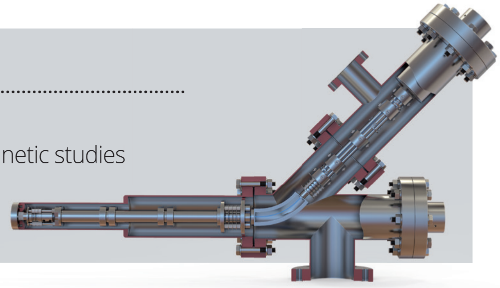


SURFACE ANALYSIS

- UHV TPD
- SIMS
- end point detection in ion beam etch
- elemental imaging – 3D mapping

PLASMA DIAGNOSTICS

- plasma source characterisation
- etch and deposition process reaction kinetic studies
- analysis of neutral and radical species



VACUUM ANALYSIS

- partial pressure measurement and control of process gases
- reactive sputter process control
- vacuum diagnostics
- vacuum coating process monitoring

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