Differential Electrochemical Mass Spectrometry
Differential Electrochemical Mass Spectrometry (DEMS)

• Electrochemistry is the interaction between electrical energy and chemical change. Electrochemical cells allow chemical reactions to be manipulated by changing the electrical conditions.
• Development of electrochemical cells is necessary to improve their performance. DEMS is a technique that can be used for mechanistic insight into the chemical reactions that occur at the electrodes.
• Using DEMS, volatile chemical species generated at the electrodes can be detected with very little time delay

Application Areas

• Fuel Cells
• Li Batteries
• Electrochemical reduction of atmospheric carbon
**Introduction to DEMS**

- Electricity is used to manipulate a chemical reaction within a cell.
- Reaction products are extracted through a membrane. Species are ionised and measured by Mass Spectrometer.
- Changing the electrode materials, electrolytes and current, etc. and getting real time analysis allows the research development of cell improvements.

Inverted Electrochemical Cell (Electrolysis)
Introduction to DEMS

- This is a typical reaction of interest. There is an equilibrium between the forward and reverse reactions, which can be influenced by applying electrical potential.

\[
\begin{align*}
\text{Forward Reaction:} & \quad \text{CH}_4 + 2\text{O}_2 & \rightarrow & \text{CO}_2 + 2\text{H}_2\text{O} \\
\text{Reverse Reaction:} & \quad \text{CO}_2 + 2\text{H}_2\text{O} & \rightarrow & \text{CH}_4 + 2\text{O}_2
\end{align*}
\]
Examples of Electrochemical Reduction Products from CO$_2$

To produce useful products from the reduction of CO$_2$ an electrochemical reaction can be utilised.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ + 2 H$^+$ + 2 e$^-$ → HCO$_2$H</td>
<td>-0.61 V</td>
</tr>
<tr>
<td>CO$_2$ + 4 H$^+$ + 4 e$^-$ → HCHO + H$_2$O</td>
<td>-0.48 V</td>
</tr>
<tr>
<td>CO$_2$ + 6 H$^+$ + 6 e$^-$ → CH$_3$OH + H$_2$O</td>
<td>-0.38 V</td>
</tr>
<tr>
<td>CO$_2$ + 8 H$^+$ + 8 e$^-$ → CH$_4$ + 2 H$_2$O</td>
<td>-0.24 V</td>
</tr>
<tr>
<td>CO$_2$ + e$^-$ → CO$_2^-$</td>
<td>-1.90 V</td>
</tr>
</tbody>
</table>

Product distribution depends on supplied voltage
DEMS - Differential Electrochemical Mass Spectrometry:

Scan the (electrochemical) potential and apply Mass Spectrometry to analyse the products

- typical scanning speeds are around 1 mV/s
- typical scanning range of 0 to -1.5 V for CO₂ Reduction

**Hiden DEMS cell types**

A. Single thin layer flow cell
B. Dual thin layer flow cell
Product Distribution vs Scanned Potential in CO$_2$ Reduction

DEMS results obtained for CO$_2$-sparged 0.05 M K$_2$CO$_3$ electrolyte (pH = 6.8) with an electrolyte flow rate of 1 mL/min and a scan rate of 0.2 mV/s. Further details are included in the ACS publication. E. L. Clark, M. R. Singh, Y. Kwon, and A. T. Bell (2015) Differential Electrochemical Mass Spectrometer Cell Design for Online Quantification of Products Produced during Electrochemical Reduction of CO$_2$. Anal. Chem., 87 (15), 8013–8020.
Hiden HPR-40 DEMS system

- Complete System including Mass spectrometer and electrochemical half cell
- Brings the speed and response of Mass Spectrometry to electrochemical research
- Standard KF fittings allows User designed cells to be connected
The Hiden DEMS System - Schematic
The Hiden DEMS System - Drawing
DEMS Cell Options

1. Type A - Single thin layer DEMS cell

2. Type B - Dual thin layer DEMS cell

3. DEMS probe for remote analysis
The thin-layer cell is an ideal approach to the study of a variety of working electrodes under static electrolyte conditions such as stripping or desorption measurements.

- Simple design
- Large surface area electrodes
Type B: Dual layer flow DEMS cell - Schematic

Dual Syringe Pump Setup

Peristaltic Pump Setup

- S. S. Frit
- Cathode
- Anode
- Peristaltic Pump
Type B: Schematic dual layer flow DEMS cell
Type B. Dual thin layer flow cell

Advantages of dual thin layer flow cell:
• good collection efficiency
• favourable electrode configuration

The dual-thin layer cell design is better suited to the monitoring of continuous faradic reactions, with controlled hydrodynamics in the determination of reaction product formation rates and turnover frequencies.

Designed by Bell et al.
Univ California Berkeley
Type B. Dual thin layer flow cell - design features

- Continuous removal of reactant products from the working electrode
- Minimises depletion of reactants at working electrode
Summary - Design

Type A. Thin layer flow cell:

+ good collection efficiency  - reactant depletion

The thin-layer cell is an ideal approach to the study of a variety of technical working electrodes under static electrolyte conditions such as stripping or desorption measurements.

Type B. Dual thin layer flow cell:

+ good collection efficiency
+ favourable electrode configuration

The dual-thin layer cell design is better suited to the monitoring of continuous faradic reactions, with controlled hydrodynamics in the determination of reaction product formation rates and turn over frequencies.

DEMS provides a powerful tool for online analysis of reactants from electrochemical reactions
Additional Evolved Gas Sampling Options

- QIC Inlet – heated capillary inlet for sampling gas at 100 mbar to 2 bar pressure
  - High/low pressure options available
  - High temperature inlets available

- Microflow inlet – for gas analysis of limited flow

- Dissolved species probes
- Flow through type
- Probe type
- Cuvette cell
- Enzyme kinetics probe
Application Data

- UC Berkeley publication


Fig. 6. (a) Comparison of the charge GITT voltage profiles with and without a catalyst obtained from Li–O$_2$ cells. (b) FT-IR measurement of electrolytes collected at the end of one cycle. Gas evolution results of Li–O$_2$ cells (c) without a catalyst and (d) with a catalyst while charging as measured by DEMS.
Academic References

• A DEMS Study of the Reduction of CO$_2$, CO, and HCHO Pre-Adsorbed on Cu Electrodes: Empirical Inferences on the CO$_2$RR Mechanism. Alnald Javier, Brian Chmielowiec, Jean Sanabria-Chinchilla, Manuel P. Šoriaga, Electrocatalysis. 6, (2) 127-131.


• Cathode Based on Molybdenum Disulfide Nanoflakes for Lithium–Oxygen Batteries, Mohammad Asadi, Bijandra Kumar, Cong Liu, Patrick Phillips, Poya Yasaei, Amirhossein Behranginia†, Peter Zapol, Robert F. Klie, Larry A. Curtiss, and Amin Salehi-Khojin, ACS Nano 2016, 10 (2) 2167-2175.
