An Electroanalytical Approach for Investigating the Reaction Pathway of Molecules at Surfaces

by Gessie Mercédes Brisard

The study of electrochemical reactions involves knowledge of various domains in chemistry and physics: thermodynamics, kinetics, electricity, transport phenomena, hydrodynamics, and so on. Therefore the fields of application of electrochemical processes are equally vast: production of electric energy from chemical reactions, production of chemical reaction from electric energy, determination of kinetics and reactions mechanisms, conception of electrical and electrochemical devices, etc. From Galvani (1786) to Faraday (1834) to Heyrovsky (1920) and Butler and Volmer (1924), many of the important laws that govern reduction-oxidation ("redox") reactions were founded. Their contributions paved the way for the popular use of electrochemical methods of analysis. Thus, electroanalytical methods, in which the passage of a current is essential to the measurement approach, are important in their own right for direct chemical analysis. However, they are very often ancillary to other analytical methods. The most commonly used response during the analysis of an electrochemical reaction is the current-potential curve I-E, the voltammogram. Voltammetry is a group of techniques in which the relation between I and E is recorded during the redox reaction, it also establishes the steady-state or transient polarization characteristics of an electrode in a reaction engaging the substance being analyzed. When during a linear-sweep voltammetry, the final potential reached (E_f) is scanned back to the original value (E_i) the technique is called cyclic voltammetry. A simple heterogeneous electron transfer reaction can be represented by Ox (aq) + e⁻ (m) ↔ Red (aq), where m denotes the electrode and aq the solution. k_{red} and k_{ox} describe the first-order heterogeneous rate constants for the reductive (forward) and oxidative (backward) electron transfer reactions. Figure 1 schematizes the cyclic voltammogram for three types of redox reactions, in which panel b) traces the I-E curve for a redox couple with a small standard rate constant.

By itself, the current-potential curve is useful but because voltammetry is an intrinsic part of the study of reaction mechanisms, it can be even more powerful when interfaced with other detection methods. Among others, mass spectrometry has been a technique of choice for many years and it all begins in the '70s with Bruckenstein *et al.*,[1-3] followed by Wolter and Heitbaum.[4,5] Numerous groups,[6-11] mainly in Europe, have used the combination of an electrochemical cell and a mass spectrometer to follow chemical reactions *in situ* and study reaction mechanisms via a technique called EC/MS (also well known as differential electrochemical mass spectrometry or DEMS). The knowledge of reaction intermediates and final products is a key point in the determination of the performance of a catalyst; therefore EC/MS is an attractive hybrid approach for this purpose. Among others, the articles of Vielstich *et al.*,[12] Baltruschat and Jusys,[13-14] and by Torresi and Wasmus[15] are very good sources of information on this topic.

Figure 2a presents a schematic of the different parts of an EC/MS setup.[15] The system can be separated into four different parts: the electrochemical cell, the interface, the vacuum chamber(s), and the mass analyzer. One of the main challenges in setting up the system is the optimization of these components in order to obtain maximum sensitivity and relatively short response time. The only experimental constraint to this technique is that the molecules to be detected and analyzed with the mass spectrometer must be able to leave the electrode surface, be volatile, and be able to be differentiated according to their fragmentation pattern.

Measurement of EC/MS profiles gives molecular specificity and permits the reaction products to be followed concurrently with electrode potential and time. The results are then displayed as a faradaic current–potential curve (obtained from the potentiostat) superimposed on a mass current–potential curve (from the mass spectrometer). Even a monolayer of CO adsorbed on a platinum surface can be detected with precision. Figure 2b is a typical result for CO_2 (m/z 44) production from the electro-oxidation of CO on a Pt surface. The top part of the figure represents the I_f –E profile (i.e., cyclic voltammogram) and the bottom part is the mass current, from the spectrometer, against the potential I_m –E (red curves of the figure).

The EC/MS approach is particularly useful for complex reaction pathways. We have recently used it to investigate the reduction of CO_2 in sulfuric
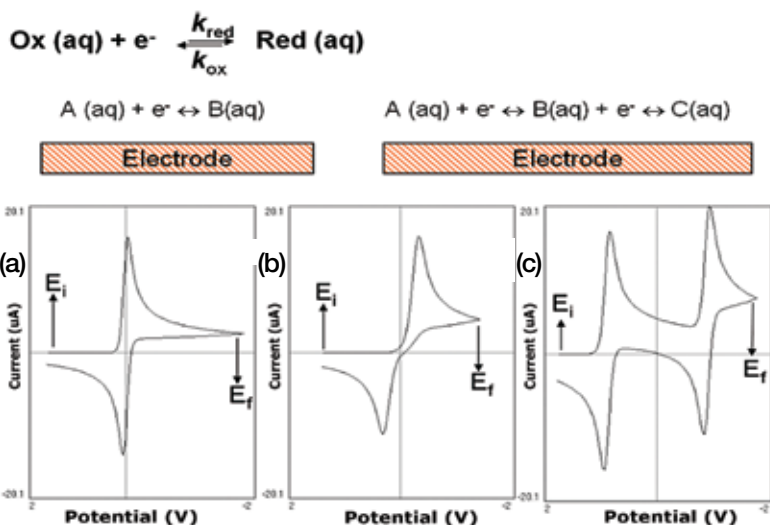

$$\text{Ox (aq) + e}^- \underset{k_{ox}}{\overset{k_{red}}{\rightleftarrows}} \text{Red (aq)}$$

A (aq) + e⁻ ↔ B(aq)   A (aq) + e⁻ ↔ B(aq) + e⁻ ↔ C(aq)

FIG. 1. *Cyclic voltammograms for (a) a fast and reversible electron transfer reaction, (b) a slow electron transfer reaction, and (c) a two-electron transfer reaction.*
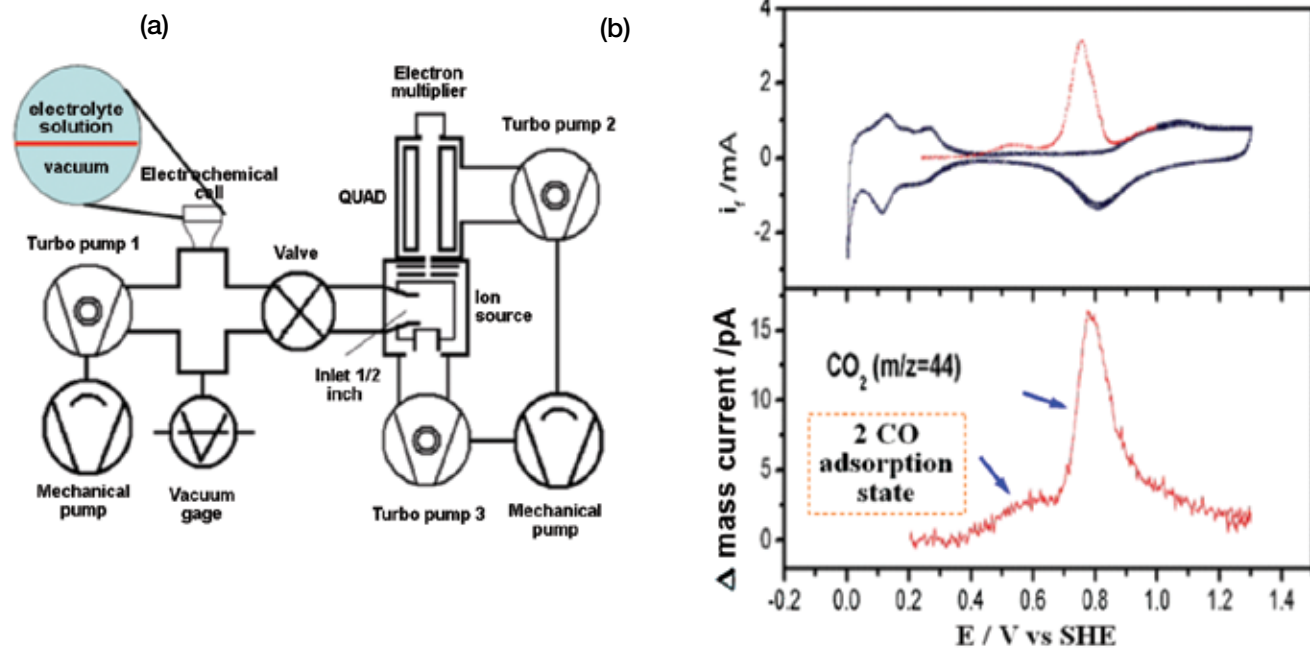
Fig. 2. *(a) Schematic of an electrochemical mass spectrometry system. (b) A typical mass spectrometric cyclic voltammetry (MSCV) for the stripping of a CO monolayer pre-adsorbed on Pt at 0.2V vs. SHE.*
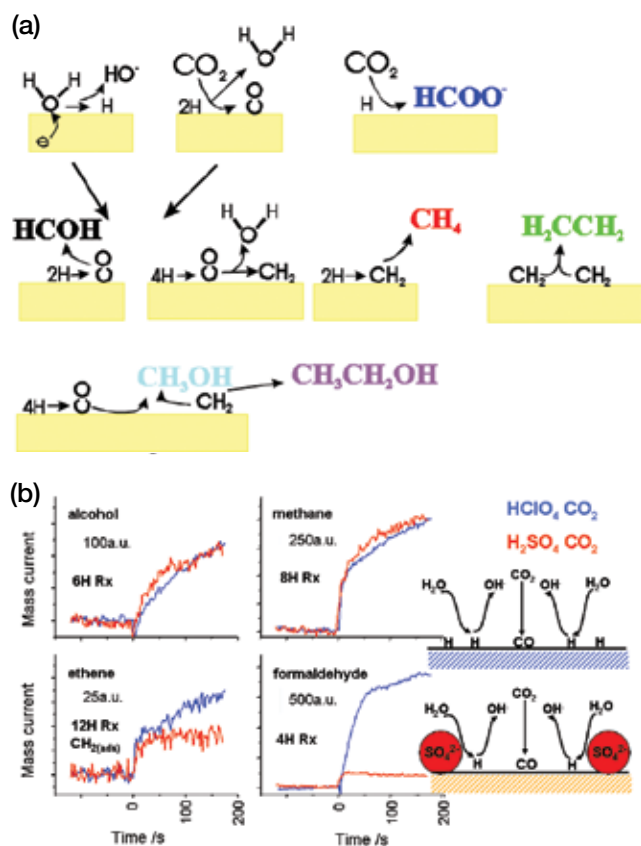

Fig. 3. *(a) Surface reactions that can occur during the electroreduction of CO_2. (b) Mass current vs. time during a potential step from -0.4V to -1.2V (vs Ag/AgCl KCl 1M) on Cu polycrystalline in CO_2 saturated solution in 0.25 M H_2SO_4 (red curve) and 0.5 M $HClO_4$ (blue curve).*

and perchloric acid electrolytes on a polycrystalline Cu surface. Gaseous products, such as CH_4, C_2H_4, and highly volatile products such as CH_3OH, HCHO, etc., are formed at overpotentials in the hydrogen evolution reaction regime. Figure 3a schematizes the various reaction pathways during CO_2 electroreduction.

The electrochemical reduction of CO_2 to generate hydrocarbon products at ambient temperatures has been seen as an attractive route for the conversion of this greenhouse gas into either potentially stored energy or as immediately available energy sources (e.g., CH_4, CH_3OH, HCOOH), in addition to providing useful precursor molecules for modern industrial chemistry applications.[16] Thus, transformation of CO_2 into more appealing molecules can be viewed as an environmentally friendly approach. An extensive review of CO_2 reduction, involving both homogeneous and heterogeneous catalysts, has been published by Sullivan.[17]

We have investigated the use of EC/MS to study this reaction in acidic media.[11] Figure 3b contains examples of the sort of valuable information that can be extracted with the on-line electroanalytical mass spectrometry method. The EC/MS setup can be a powerful tool to study the products from CO_2 and CO electrocatalytic reduction processes. It has been shown that the electrolyte composition affects the formation and production rate for the four major products that have been detected. The results suggest that the formation of methane and formaldehyde are kinetically faster than ethene and alcohol on copper in both electrolytes. The initial surface state of the electrocatalyst, modified by anion adsorption, plays a role in determining the potential where HCHO formation occurs on copper. It is suggested that the electroreduction of CO_2 and CO occurs via an electrocatalytic hydrogenation process.[11]

This tutorial provides a brief glimpse of the possibilities from combining an electroanalytical technique such as voltammetry with an analytical workhorse such as mass spectrometry. The EC/MS hybrid technique is illustrated with data on the electro-oxidation of CO on Pt and the electroreduction of CO_2 on polycrystalline Cu surfaces. ∎

References

1. S. Bruckenstein and J. Comeau, *Faraday Disc. Chem. Soc.*, **56**, 285 (1974).
2. L. Grambow and S. Bruckenstein, *Electrochim. Acta*, **22**, 377 (1977).
3. S. Bruckenstein and J. Comeau, *Faraday Disc. Chem. Soc.*, **56**, 285 (1974).
4. O. Wolter and J. Heitbaum, *Ber. Bursenges. Phys. Chem.*, **88**, 2 (1984).
5. O. Wolter and J. Heitbaum, *Ber. Bursenges. Phys. Chem.*, **88**, 10 (1984).
6. S. Wasmus, S. R. Samms, and R. F. Savinell, *J. Electrochem. Soc.* **142,** 1183 (1995).
7. P. Bogdanoff, P. Friebe, and N. Alonso-Vante, *J. Electrochem. Soc.*, **145**, 576 (1998).
8. Z. Jusys, H. Massong, and H. Baltruschat, *J. Electrochem. Soc.*, **146,** 1093 (1999).
9. R. Stadler, Z. Jusys, and H. Baltruschat, *Electrochim. Acta*, **47**, 4485 (2002).
10. K. Jambunathan, S. Jayaraman, and A. C. Hillier, *Langmuir*, **20,** 1856 (2004).
11. P. Dubé and G. M. Brisard, *J. Electroanal. Chem.,* **582**, 230, (2005).
12. B. Bittins-Cattaneo, E. Cattaneo, P. Königshoven, and W. Vielstich, *Electroanalytical Chemistry*, Vol. 17, p. 181, A. J. Bard, Editor, Marcel Dekker, New York, (1991).
13. H. Baltruschat, *Interfacial Electrochemistry: Theory, Experiment, and Application*, Chapter 33, A. Wieckowski, Editor, Marcel Dekker, New York (1999).
14. H. Baltruschat, *J. Am. Soc. Mass Spectrom.*, **15**, 1693 (2004).
15. R. M. Torresi and S. Wasmus, *Handbook of Fuel Cells: Fundamentals, Technology, and Applications, Volume 2: Electrocatalysis*, Chapter 15, W. Vielstich, H. A. Gasteiger, A. Lamm, Editors, John A. Wiley & Sons, New York, (2003).
16. B. P. Sullivan, *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*, Elsevier, Amsterdam (1993).

About the Author

Gessie Brisard received her PhD in non-aqueous electrochemistry in 1990 from the Université de Sherbrooke (Canada). After her postdoctoral studies at Lawrence Berkeley National Laboratory (U.S.) in 1992, she was appointed assistant professor in the chemistry department of the Université de Sherbrooke and became full professor in 2004. She has developed research programs in the fields of electrocatalysis (namely structure–sensitivity of electroreduction processes) and electroanalytical chemistry. Gessie Brisard has been an active member of ECS since 1989. She was chair of the ECS Canadian Section in 1997 and is presently serving as chair of the ECS Physical and Analytical Electrochemistry Division. She may be reached at Gessie. Brisard@USherbrooke.ca.

the University of Colorado College of Music and the Colorado Music Festival. He endowed a professorship and student scholarships in the Department of Materials Science and Engineering at the University of Illinois.

He was preceded in death by his first wife, Lotte Oettinger Thurnauer (d. 1959); his second wife, Elba Dolores Benedict Thurnauer (d. 2001); and his son, Peter Thurnauer (d. 1976). He is survived by his daughters: Dorothy Kaplan and husband Donald (Kensington, CA), Marion Thurnauer and husband, Alexander Trifunac (Boulder); six grandchildren: Thomas, Eric, Monica, and Marita Thurnauer, and Andrew and Timothy Kaplan; two great-grandchildren: Frances and Cole Thurnauer-Montesano; and daughter-in-law Milena Renshaw. ∎

THE ELECTROCHEMICAL SOCIETY MONOGRAPH SERIES

The following volumes are sponsored by ECS, and published by John Wiley & Sons, Inc. They should be ordered from: ECS, 65 South Main St., Pennington, NJ 08534-2839, USA.

Fundamentals of Electrochemical Deposition (2nd Edition)
Edited by M. Paunovic and M. Schlesinger (2006)
373 pages. ISBN 0-471-71221-3.

Fundamentals of Electrochemistry (2nd Edition)
Edited by V. S. Bagotsky (2005)
722 pages. ISBN 0-471-70058-4.

Electrochemical Systems (3rd edition)
by John Newman and Karen E. Thomas-Alyea (2004)
647 pages. ISBN 0-471-47756-7.

Modern Electroplating (4th edition)
by M. Schlesinger and M. Paunovic (2000)
832 pages. ISBN 0-471-16824-6.

Atmospheric Corrosion (2nd edition)
by C. Leygraf and T. Graedel (2000)
354 pages. ISBN 0-471-37219-6.

Uhlig's Corrosion Handbook (2nd edition)
by R. Winston Revie (2000)
1300 pages. ISBN 0-471-15777-5.

Semiconductor Wafer Bonding
by Q. -Y. Tong and U. Gösele (1998)
297 pages. ISBN 0-471-57481-3.

Fundamentals of Electrochemical Deposition
by M. Paunovic and M. Schlesinger (1998)
301 pages. ISBN 0-471-16820-3.

Corrosion of Stainless Steels (2nd edition)
by A. J. Sedriks (1996)
437 pages. ISBN 0-471-00792-7.

Synthetic Diamond: Emerging CVD Science and Technology
Edited by K. E. Spear and J. P. Dismukes (1994)
688 pages. ISBN 0-471-53589-3.

Electrochemical Oxygen Technology
by K. Kinoshita (1992)
444 pages. ISBN 0-471-57043-5.

ECS Members will receive a discount. Invoices for the cost of the books plus shipping and handling will be sent after the volumes have been shipped. All prices subject to change without notice.