Int. J. Electrochem. Sci., 1(**2006**)379-382

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Setting the Record Straight on Reciprocal Derivative Chronopotentiometry

D. Britz

Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Århus C, Denmark
E-mail: britz@chem.au.dk

Received: 20 *September* 2006 / *Accepted:* 9 October 2006 / *Published:* 1 November 2006

Mention of the technique "reciprocal derivative chronopotentiometry" is often accompanied by a reference to Jagner (1983), but this is not the original source of the technique, which was described in six earlier publications. Likewise, the term itself is often attributed to a 1996 source, but in fact dates back to 1988. Thirdly, the idea of derivative chronopotentiometry is attributed to a 1966 source but stems from a 1959 paper.

Keywords: Stripping analysis, chronopotentiometry, derivative chronopotentiometry

Chronopotentiometry has been known since 1900 [1–3]. In this technique, a controlled current (often constant) is applied to an electrode, and the electrode potential is plotted against time (see such standard texts as Bard & Faulkner [4] or Galus [5] for details). Herman and Bard [6] then introduced cyclic chronopotentiometry, in which the sign of the current is switched at regular intervals.

There are some practical problems with obtaining an analytical signal from a chronopotentiogram, this being the transition time [1,2,4,5], at which time the concentration of the electroactive substance has just reached zero at the electrode. The potential is here seen to change from a relatively flat function of time to a steeper function, as another electroactive species takes up the current. In 1959, Iwamoto [7] therefore suggested recording not the potential E, but its derivative with time dE/dt, against time. This paper was later referred to by Sturrock [8], who combined the derivative idea with cyclic chronopotentiometry [6]. Derivative chronopotentiometry is nevertheless often credited to Peters and Burden [9] (for example, [10–15]), and Peters and Burden did not cite Iwamoto or Sturrock.

Derivative chronopotentiometry, as this technique is called, yields curves with a minimum in the middle of the time range, and the transition time is now the length of time between the two steep ends of the function, which is more convenient, but can still be improved upon. Such an improvement was made (instrumentally) by Mortensen et al [16] in 1979, followed by further publications from the

same group (which will now be called the Kryger group here) over the next years [17–21]. These papers all dealt with the technique of potentiometric stripping analysis (PSA), devised by Jagner and Graneli in 1976 [22]. If one widens the term "chronopotentiometry" to denoting a technique in which a certain (not necessarily constant) current flows at an electrode and the electrode potential is monitored with time, then PSA falls under this term. As has been shown [21], in PSA, at the point at which the deposition current is switched off, the chemical oxidiser (for example, Hg^{2+} ions), which up to that time has been codeposited (or, generally, reduced) now acts as an electron sink and reoxides the metal deposit. The double layer capacity is slowly discharged and the effective oxidising current decreases with time. As with constant current chronopotentiometry, the potential is the signal. The novelty of the 1979 paper [16] and the follow-up papers was that the signal is, effectively, dt/dE either vs. time or potential. This was not explained in these terms but was explained as an instrumental method, called "multichannel [chronopotentiometry]". It was achieved by means of slotting the electrode potential into ranges and measuring the length of time the signal remains within these ranges [16–21] The resulting plot is a discrete approximation of the dt/dE signal. It can be plotted either against time or potential, and it is the area under the peak-shaped curve that is the analytical signal.

These publications are rarely cited (although they have been [23–28]). Instead, a paper by Jagner written in 1983 [29] is usually cited (an SCI search found about 50 such citations), and these earlier works are largely overlooked. In the Jagner paper, there is no description of the technique, which appears only in two figures as an axis marked with " $dt(dE)^{-1}$". The purpose of this communication is to point out the earlier papers [16–21], which should be cited in this context.

The technique was given a new name, "reciprocal derivative chronopotentiometry", in 1988 by Ruan and Chang [14], who do not cite the Kryger group papers, and in fact not the Jagner paper of 1983 either. One can also point to an earlier paper by Nishida et al. in 1984 [15], who used this term, applying it however to the reciprocal of $dE/d\sqrt{t}$. These authors have been cited only once, by themselves [30]. Ironically, the paper by Ruan and Chang too appears to have been forgotten, and the term is mostly attributed to a later paper by Bi et al. [31], see for example [12] (there are other citations).

A Chemical Abstracts search on the words "reciprocal derivative chronopotentiometry" found 27 hits [10-15,31-51] (including some of the above cited works), and of these, 14 cite Bi et al [31], 5 cite Ruan et al [14] (two of these are by Ruan et al themselves) and 5 cite Jagner 1983 [29]. As mentioned above, Peters and Burden [9] are cited 6 times.

It is hoped that this communication will set the record straight on these developments and their history.

References

1. H.J. S. Sand, *Z. phys. Chem.* 35 (1900) 641.
2. H.J. S. Sand, *Phil. Mag.* (1901) 45.
3. Z. Karaoglanoff, *Z. Elektrochem.* 12 (1906) 5.
4. A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, John Wiley, New York, 2001.

5. Z. Galus, *Fundamentals of Electrochemical Analysis*, Ellis Horwood, New York, 2 edition, 1994, transl. Eds. R.A. Chalmers & W.A.J. Bryce.
6. H. B. Herman, A. J. Bard, *Anal. Chem.* 35 (1963) 1121.
7. R. T. Iwamoto, *Anal. Chem.* 31 (1959) 1062.
8. P. E. Sturrock, *J. Electroanal. Chem.* 8 (1964) 425.
9. D. G. Peters, S. L. Burden, *Anal. Chem.* 38 (1966) 530.
10. A. Molina, J. Gonzalez, M. M. Moreno, *Electroanalysis* 14 (2002) 281.
11. S. Bi, J. Chen, L. Ye, T. Chen, S. Du, *Nanjing Daxue Xuebao, Ziran Kexue* 36 (2000) 243, in Chinese.
12. L. M. Abrantes, J. Gonzáles, A. Molina, *Electrochim. Acta* 45 (1999) 457.
13. X. Ruan, X. Chang, *Huaxue Xuebao* 49 (1991) 65, in Chinese.
14. X. Ruan, H. Chang, *Talanta* 35 (1988) 861.
15. M. Nishida, N. Kato, K. Nakano, *J. Electroanal. Chem.* 164 (1984) 189.
16. J. Mortensen, E. Ouziel, H. J. Skov, L. Kryger, *Anal. Chim. Acta* 112 (1979) 297.
17. J. K. Christensen, L. Kryger, *Anal. Chim. Acta* 118 (1980) 53.
18. J. K. Christensen, L. Kryger, J. Mortensen, J. Rasmussen, *Anal. Chim. Acta* 121 (1980) 71.
19. L. Kryger, *Anal. Chim. Acta* 120 (1980) 19.
20. H. J. Skov, L. Kryger, *Anal. Chim. Acta* 122 (1980) 179.
21. J. Mortensen, D. Britz, *Anal. Chim. Acta* 131 (1981) 159.
22. D. Jagner, A. Graneli, *Anal. Chim. Acta* 83 (1976) 19.
23. T. M. Florence, *J. Electroanal. Chem.* 168 (1984) 207.
24. Y. Zie, C. O. Huber, *Anal. Chim. Acta* 263 (1992) 63.
25. S. Komorsky-Lovric, M. Branica, *Anal. Chim. Acta* 276 (1993) 361.
26. H. P. Beck, T. Schiestel, *Fresenius J. Anal. Chem.* 356 (1996) 123.
27. Y. Bai, X. Ruan, J. Mo, Y. Xie, *Anal. Chim. Acta* 373 (1998) 39.
28. R. M. Town, H. P. van Leeuwen, *J. Electroanal. Chem.* 509 (2001) 58.
29. D. Jagner, *Trends Anal. Chem.* 2 (1983) 53.
30. K. Nakano, N. Kato, M. Nishida, Y. Tanaka, M. Nakanishi, S. Fujieda, *Bunseki Kagaku* 34 (1985) 686.
31. S. Bi, J. Yu, *J. Electroanal. Chem.* 405 (1996) 51.
32. S. Bi, J. Chen, T. Chen, *Coll. Czech. Chem. Commun.* 65 (2000) 971.
33. S. Bi, J. Chen, X. Xing, J. Yu, *Coll. Czech. Chem. Commun.* 65 (2000) 963.
34. S. Bi, H. Gao, Y. Sun, *Nanjing Daxue Xuebao, Ziran Kexue* 30 (1994) 464, in Chinese.
35. S. Bi, X. Xing, J. Chen, S. Du, in Book of Abstracts, 212th ACS National Meeting, Orlando, FL, 25–29, American Chemical Society, Washington, D.C., 1996.
36. S. Bi, J. Yu, in Book of Abstracts, 210th ACS National Meeting, Chicago, IL, 20–24, American Chemical Society, Washington, D.C., 1995.
37. S. Bi, J. Yu, L. Ye, B. He, *Instr. Sci. Technol.* 28 (2000) 303.
38. L. Chen, Z. Wang, X. Lu, W. Han, S. Bi, *Electrochim. Acta* 51 (2006) 5548.
39. J. Gonzalez, A. Molina, Port. *Electrochim. Acta* 19 (2001) 337.
40. J. Gonzalez, A. Molina, *Langmuir* 17 (2001) 5520.
41. J. Gonzalez, A. Molina, M. Lopez-Tenes, C. Serna, *J. Electrochem. Soc.* 147 (2000) 3429.
42. M. Lopez-Tenes, J. M. Molina, A. Molina, *Electroanalysis* 16 (2004) 938.
43. M. Lopez-Tenes, I. Morales, A. Molina, *Electrochim. Acta* 51 (2006) 2851.
44. A. Molina, J. Gonzalez, *Electrochem. Commun.* 1 (1999) 477.
45. A. Molina, J. Gonzalez, *J. Electroanal. Chem.* 493 (2000) 117.
46. A. Molina, J. Gonzalez, *Langmuir* 19 (2003) 406.
47. A. Molina, J. Gonzalez, I. Morales, *Electroanalysis* 17 (2005) 674.
48. A. Molina, J. Gonzalez, F. Saavedra, L. M. Abrantes, *Electrochim. Acta* 45 (1999) 761.
49. X. Ruan, J. Li, Y. Li, J. Deng, *Chinese Chem. Lett.* 3 (1992) 205.

50. X. Ruan, Y. Su, Y. Zhou, H. Chang, D. Feng, *Talanta* 43 (1996) 1657.
51. J. Wang, B. Tian, *Anal. Chem.* 72 (2000) 3241.