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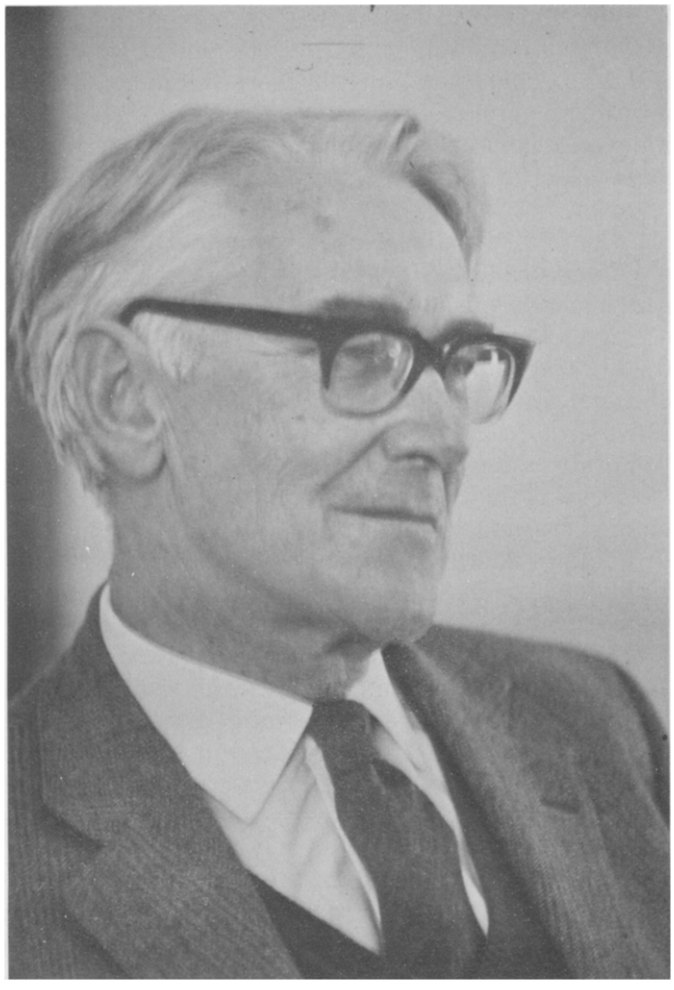

GEOFFREY C. BARKER

Geoffrey Barker was born on 2nd October 1915 and in 1933 became a medical student at Cambridge, where he was a member of Gonville and Caius College. After gaining his bachelor's degree in 1936 he switched to chemistry for his Part II year, following which he became a research student under the late F.P. Bowden. At that time Bowden was still pursuing the electrochemical interests which he had developed ten years earlier with Rideal. Nevertheless, Barker's work combined these with Bowden's newer interest in friction and he studied the electrochemical behaviour of platinum and its relation to the friction between two platinum surfaces. He gained his M.A. in 1939 but the research was then interrupted by the war.

In 1940 Barker joined the constellation of academic stars applying science to the prosecution of the war. At this time he learned electronics thorougly and took part in radar development at Swanage and at the Telecommunications Research Establishment at Great Malvern where he became Section Leader of the group responsible for anti-jamming devices for ground radar and navigational aids; later they developed the first, very crude, Doppler radar. He then became leader of the Special Display Group which developed the detection systems which enabled the distinction between V1 weapons and aircraft within 4 days of the advent of the former. They also developed detectors for V2 and displays for use in the Far East. With the rank of Wing Commander he served briefly with the RAF in Malta, Egypt and Germany.

After directing such a large group it is remarkable that at the end of the war he returned to the laboratory, being seconded from TRE back to Bowden's team in Cambridge, where he undertook the supervision of one man, L. Young. Very soon, however, he went to Canada where, from 1946 to 1950, he worked at the CRC Laboratory in Chalk River, Ontario. Here he laid the foundations for his later work using the two major interests of electrochemistry and electronics. He studied the photoconduction of anodic films on Hg, the adsorption of hydrogen on Pt and the oxidation of hydrogen on Hg as well as developing the first bi-directional potentiostat. At this time he made substantial plans for his future work, much of which was achieved during his 25 years at Harwell from 1950 to 1975. There he did much of the experimental work himself, working with only a very small number of research associates whose names appear in the reference list. Later some research associates from overseas joined him, first H.W. Nürnberg from Germany in 1962, followed by J.A. Bolzan from Argentina and eventually G. Bottura and V. Concialini and O. Tubertini from Italy. His collaboration with the group in Bologna still continues.

Geoffrey Barker's major achievements may be briefly outlined in order to fill out to some extent the bare bones of the reference list.

In 1952 invented *square wave polarography*, showing the practical use of the different time laws for the capacitance and faradaic current components. This enables the extension of the sensitivity down to 10^{-8} *M*. The first commercial square wave polarograph was developed by Mervyn Instruments on the basis of his design. It may also be noted that at this time [3] he described *anodic stripping* for the first time, indicating the great power of this method which has now proved itself in many applications.

In 1958 he gave a very important invited paper [20] to a Conference on Electroanalytical Chemistry in Paris. This described not only SWP but also the new method of *radio frequency polarography* where for the first time faradaic rectification is used in a reliable and powerful second order polarographic method. His famous paper on faradaic rectification [26] was presented at some length during the Electrochemical Society's Symposium in Philadelphia in 1959. It is one of his most difficult yet rewarding papers. No doubt with this in mind Reinmuth was later to advocate to the aspiring electrochemist an annual reading of Barker's papers. This paper reveals the potential of this

method for the study of electrode processes as well as making clear that in the context of RF polarography Barker had introduced the *Coulostatic method* long before Delahay and Reimuth.

Pulse polarography was described with Gardner in 1958 at an International Polarographic Symposium in Bonn. This method has become the most important of the advanced polarographic methods because of its versatility and its approximately equal sensitivity for reversible and irreversible systems. The first commercial instrument was developed by Southern Analytical, but unfortunately little significant investment was made into further development and with the advent of integrated circuits the field has now been taken over by Princeton Applied Research using the simpler and somewhat less versatile design due to Osteryoung.

Barker's contribution [21] to the Polarographic Congress at Cambridge in 1959 is noteworthy for the development of modern a.c. methods, as well as for the measurement of double layer capacities. He also described an ingenious method to suppress efficiently the capacity current in conventional d.c. polarography.

In 1962—63 Barker and Nürnberg developed *high level faradaic rectification*, a polarographic second order technique with large amplitude pulses using the coulostatic principle for polarisation and the faradaic rectification effect to separate the faradaic response. Using μs pulses, they were able to study very fast electrode reactions and coupled homogeneous chemical reactions. They also developed a new version of RF polarography with superimposed SW component. This method is mentioned in a recent review [73] but has still to be fully published; it is incorporated as one mode in Barker's new *multi-mode polarograph* [55,56]. This mode is particularly efficient for the separation of electrode processes occurring at closely spaced potentials.

In 1964 Barker presented [36] the principles of new non-linear relaxation methods which formed other modes of the multi-mode polarograph. These are *square wave intermodulation*, and *modulation polarography* (high frequency version). The latter has led to the elucidation of the problems of adsorbed species in an electrode process and of adsorbed biological macromolecules [77].

More recently he has written on the potentialities of methods such as noise [43,49], a.c. polarography with triangular waves [52], the processing of polarographic responses [62] and a temperature perturbation method [76]. Nevertheless in the last 15 years Barker has made more and more use of the techniques he has developed to study fundamental problems particularly rather complex ones on electrodes. One important example of this is the paper [30] presented at the Gesellschaft Deutscher Chemiker at Bonn in 1965 on the specific adsorption of depolarisers, using improved conventional d.c. and a.c. polarography, SWP, pulse polarography and RF polarography.

A larger field of his fundamental work concerns the photoemission of electrons from electrodes and their subsequent reaction. Although an accident prevented his attending the CITCE meeting in Moscow in 1963 the paper he sent to

that meeting [35] originated the modern work on photoelectrochemistry. In a later and better known paper given at the Cleveland Symposium of the Electrochemical Society in 1966 he described the ingenious way in which he synchronised the light pulses emitted by the Xenon lamp with pulse polarographic polarisation of the electrode to establish well-defined conditions of electron emission. His work advanced significantly the understanding of the behaviour and scavenging kinetics of solvated electrons and confirmed results obtained by pulse radiolysis.

Geoffrey Barker's co-workers report that his attitude towards experiments is always very critical and suspicious; they were carefully watched for a time before the results were accepted. He is an excellent and inspired teacher in long and comprehensive personal discussions. It is unfortunate that more students have not been able to benefit from this guidance up to now. Although he expresses his opinions modestly, he has strong and well thought out views on the achievements of his colleagues in the electrochemical world. For him the design of techniques was always only a means to the end of the elucidation of important unsolved fundamental problems. Nevertheless electronics design work of an advanced level attracts him in an aesthetic sense and this is evident in his elegant designs.

Since he retired from Harwell, Geoffrey Barker has been appointed an Honorary Research Fellow in the School of Chemistry at Bristol where he hopes to continue his fundamental work. His friends and colleagues throughout the world wish him a productive future there and look forward to many more exciting ideas from his fertile brain.

PUBLISHED WORKS OF G.C. BARKER

1 The platinum electrode; the overpotential of metals. Thesis (Cambridge) 1947.
2 The automatic control of electrode potential. CRC -440 (1950).
3 with I.L. Jenkins, Square Wave Polarography. Analyst, 77 (1952) 920.
4 with I.L. Jenkins, Square Wave Polarography, Part I — General Introduction. A.E.R.E. C/R 924 (1952).
5 with D.R. Cockbaine, Square Wave Polarography, Part II — Notes on the Use of the Square Wave Polarography. A.E.R.E. C/R 1404 (1954).
6 Square Wave Polarography, Part III — Single Drop Polarography. A.E.R.E. C/R 1563 (1954).
7 with H. Small, The Electrochemistry of Ion Exchangers, Part I — The Electrical Conductivity of Certain Resinates of Dowex 50. A.E.R.E. C/R 1504.
8 with H.Small, The Electrochemistry of Ion Exchangers, Part II — Electromigration in Dowex 50 Resinates. A.E.R.E. C/R 1505 (1954).
9 The Measurement of Interfacial Impedances. A.E.R.E. C/R 1565 (1965).
10 with A.W. Gardner, Diffusion and Reaction at the Dropping Mercury Electrode. A.E.R.E. C/R 1513 (1954).
11 The Motion of Ions near the Surface of a Polarized Ion Exchange Membrane. A.E.R.E. C/R 1547 (1954).
12 The Influence of Non-uniform Mercury Flow and Intermittent Polarization on the Diffusion Current. A.E.R.E. C/R 1553 (1954).

13 An electrocapillary Valve for Controlling Mercury Flow to a Dropping Mercury Electrode. C/R 1567 (1954).
14 with A.W. Gardner and R.L. Faircloth, Square Wave Polarography, Part IV — An Introduction to the Theory of Square Wave Polarography. A.E.R.E. C/R 1786 (1955).
15 with A.W. Gardner, Square Wave Polarography, Part V — Organic Adsorption-Desorption Waves. A.E.R.E. C/R 1606 (1955).
16 with R.L. Faircloth, Square Wave Polarography, Part IV — Polarographic Behaviour of Metallic Ions in Molten Nitrates. A.E.R.E. C/R 2032 (1956).
17 with G.W.C. Milner and H.I. Shalgosky, Polarography. Proc. of Congress on Modern Analytical Chem. in Industry, St. Andrews, 1957, p. 199.
18 with R.L. Faircloth and A.W. Gardner, Use of Faradaic Rectification for the Study of Rapid Electrode Processes. Nature, 181 (1958) 247.
19 with A.W. Gardner, Pulse Polarography. A.E.R.E. C/R 2297 (1958).
20 Square Wave Polarography and Some Related Techniques. Anal. Chim. Acta, 18 (1958) 118.
21 Some Possible Developments in A.C. Polarography. Proc. 2nd Intl. Congress of Polarography, Cambridge, 1959, Pergamon, Oxford, 1960, p. 144.
22 with R.L. Faircloth, The Double layer Capacity of Mercury in Contact with Concentrated Electrolyte Solutions. ibid., p. 313.
23 with A.W. Gardner, The Effect of the Back Pressure in Polarography. ibid., p. 330.
24 with A.W. Gardner, Pulse Polarography. Z. Anal. Chem., 173 (1960) 79.
25 with G.W.C. Milner, Polarography. Endeavour, Vol. XX, No. 77 (1961) pp. 26—31.
26 Faradaic Rectification. In E. Yeager (Ed.), Trans. Symp. on Electrode Processes, Philadelphia, 1959, Wiley, New York, 1961, pp. 325—364.
27 with H.W. Nürnberg, High Level Faradaic Rectivication. I — General Principles; II — Application to Fast Charge Transfer Reactions and Coupled Chemical Reactions. Abstracts CITCE Meeting, Rome, 1962, in course of publication.
28 with H.W. Nürnberg, On the Study of Very Rapid Homogeneous Chemical Reactions by New Electrochemical Methods. Naturwiss., 51 (1964) 191.
29 with H.W. Nürnberg, The Determination of the Rate Constants for the Dissociation and Recombination of Weak Acids by High Level Faradaic Rectification. Ibid., p. 192.
30 with J.A. Bolzan, Effects in Polarography Attributable to Specific Adsorption of Depolarizers. Z. Anal. Chem., 216 (1966) 215.
31 Square Wave and Pulse Polarography. in P. Zuman (Ed.), Progress in Polarography, Interscience, New York, 1962, p. 411.
32 with H.W. Nürnberg and J.A. Bolzan, The Study of Irreversible Processes by Modern Instrumental Methods, Jül 137 Ga (1963) (in English); Osnovne voprosy sovremennoi teoret elektrochimi, Mir, Moscow, 1965 (in Russ.).
33 Aperiodic Equivalent Circuits for the Faradaic Impedance. Osnovne voprosy sovremenoi teoret elektrochimi, Mir, Moscow, 1965, pp. 42—90 (in Russ.).
34 Aperiodic Circuits for the Faradaic Impedance. A.E.R.E. HaR 3064 (1963) (digest of 32 in Engl.).
35 with A.W. Gardner, Photocurrents Produced by UV Irradiation of Mercury Electrodes; Part I — Reactions between Hydrogen Ions and Hydrated Electrons. Osnovne voprosy sovremennoi teoret elektrochimi, Mir, Moscow, 1965, pp. 34—42 (in Russ.); A.E.R.E. HaR 3063 (1963) (in Engl.).
36 Non-linear Relaxation Methods for the Study of Very Fast Reactions. in G.J. Hills, (Ed.), Polarography 1964, Macmillan, London, 1966.
37 The Equivalent Circuit for the Electrical Double Layer. J. Electroanal. Chem., 12 (1966) 495.
38 with A.W. Gardner and D.S. Sammon, Photocurrents Produced by UV Irradiation of Mercury Electrodes; Part II — Factors Influencing Photocurrents Produced by Electron Emission. J. Electrochem. Soc., 113 (1966) 1182—1197.

39 Theory of The Current in a.c. Polarography. Pure and Appl. Chem., 15 (1967) 239.
40 with D.C. Sammon, Kinetics of Proton Transfer Reactions. Nature, 213 (1967) 65.
41 The Influence of Ethanol on the Nitrous Oxide and Hydrogen Ion Photocurrents at a Mercury Electrode. Electrochim. Acta, 13 (1968) 1221.
42 with B. Stringer and M.J. Williams, Application of Short Duration Light Pulses to the Study of the Nitrous Oxide Photocurrent at a mercury Electrode. A.E.R.E. R 6207 (1969).
43 Noise Connected with Electrode Processes. J. Electroanal. Chem., 21 (1969) 127.
44 with P. Fowles, D.C. Sammon and B. Stringer, Pulse Radiolytic Induced Transient Electrical Conductance in Liquid Solutions; Part I — Technique and the Radiolysis of Water. Trans. Faraday Soc., 66 (1970) 1498.
45 with P. Fowles and B. Stringer, Pulse Radiolytic Induced Transient Electrical Conductance in Liquid Solutions; Part II — Radiolysis of Aqueous Solutions of NO_3^-, NO_2^- and $Fe(CN)_6^{3-}$. ibid., 1509.
46 with P. Fowles, Pulse Radiolytic Induced Transient Electrical Conductance in Liquid Solutions; Part III — Radiolysis of Aqueous Solutions of some Inorganic Systems. ibid., 1661.
47 Electrochemical Effects Produced by Light-induced Electron Emission. Ber. Bunsenges. Phys. Chem., 75 (1971) 728.
48 A Preliminary Search for Interfacial Light Absorption Caused by Faradaic Electron Transfer. J. Electroanal. Chem., 39 (1972) 480.
49 Flicker Noise Connected with the Hydrogen Evolution Reaction on Mercury. J. Electroanal. Chem., 39 (1972) 484.
50 The Influence of Interactions between Electrode Processes on the Structure of the Equivalent Electrical Circuit for the Electrode-solution Interface. J. Electroanal. Chem., 40 (1972) 45.
51 with A.W. Gardner, The Influence of Polyvalent Ions on Interfacial Impedance. Chim.-Ing. Techn., 44 (1972) 211.
52 Developments in a.c. Polarography and Electrochemical Perturbation Techniques; Part I — Triangular Wave Polarography. J. Electroanal. Chem., 41 (1973) 95.
53 Aperiodic Circuits for the Electrolyte Solution and the Ideally Polarizable Electrode and for the Ion and its Atmosphere. J. Electroanal. Chem., 41 (1973) 201.
54 The Influence of Surface Curvature on the Faradaic Impedance. J. Electroanal. Chem., 41 (1973) App. 1.
55 with A.W. Gardner and M.J. Williams, A Multiple-mode Polarograph. J. Electroanal. Chem., 42 (1973) App. 21.
56 Some developments in Polarographic Instrumentation. Anglo-Czech Electrochemcial Symposium, London (1973), in course of publication.
57 Equivalent Circuits for a Cell Affected by Space Charge in the Solution and Simple Reactions at the Electrodes. J. Electroanal. Chem., 44 (1973) 473.
58 with G. Bottura and A.W. Gardner, Laser-induced Potential Changes at a Mercury Electrode. J. Electroanal. Chem., 45 (1973) 21.
59 with V. Concialini, Competition between H_3O^+ and N_2O for Hydrated Photo-electrons. J. Electroanal. Chem., 45 (1973) 320.
60 with V. Concialini, Anodic Photocurrents Produced by the Heterogeneous Photolysis of Oxalate Ions. J. Electroanal. Chem., 46 (1973) 25.
61 with G. Bottura, The Influence of Formate Ions on the Nitrous Oxide Photocurrent. J. Electroanal. Chem., 46 (1973) 35.
62 with A.W. Gardner, The Processing of Polarographic Waves. J. Electroanal. Chem., 46 (1973) 150.
63 with G. Bottura, Slow Faradaic Processes Following Homogeneous Electron Capture. J. Electroanal. Chem., 47 (1973) 199.
64 with A.W. Gardner, The Temporal Variation of Photocurrent for a Light Step and an Electrochemically Inert Adduct. J. Electroanal. Chem., 47 (1973) 205.

65 with G. Bottura, V. Concialini, D. McKeown and M.J. Williams, Charge Transfer Reactions Involving Intermediates formed by Homogeneous Capture of Laser-produced Photoelectrons. Faraday Soc. Disc., 56 (1973) 41.
66 with J.A. Bolzan, The Influence of Homogeneous Hydrogen Abstraction on the Nitrous Oxide Photocurrent; Part I — Underlying Theory. Part II — Suppression by Aliphatic Alcohols. J. Electroanal. Chem., 49 (1974) 227, 239.
67 with A.W. Gardner, Comment on "The Photo-electric Effect at the Metal-Electrolyte Boundary. Elektrokhimiya, 2 (1973) 1684.
68 with G. Bottura, G. Cloke, A.W. Gardner and M.J. Williams, The Influence of the Plane of Polarization on the Photoemission of Electrons. J. Electroanal. Chem., 50 (1974) 323.
69 with B. Stringer and M.J. Williams, The Determination of Electron Capture Rate Constants by the Study of Photocurrent Systems in the Non-steady State. J. Electroanal. Chem., 51 (1974) 305.
70 with J.A. Bolzan and A.W. Gardner, The Indirect Determination of Differential Capacity by High Frequency Modulation Polarography. J. Electroanal. Chem., 52 (1974) 193.
71 with G. Cloke, Electrical Double Layer Perturbation by Light Absorption at the Interface. J. Electroanal. Chem., 52 (1974) 468.
72 with V. Concialini and O. Tubertini, Photocurrents Produced by Sulphur Hexafluoride in Aqueous Solutions. J. Electroanal. Chem., 57 (1974) 413.
73 Modern Polarographic Techniques. Proc. Anal. Divn. Chem. Soc., 12 (1975) 179.
74 with D. McKeown, Kinetics of Aniline Adsorption-Desorption on Mercury. J. Electroanal. Chem., 59 (1975) 295.
75 with D. McLeown, Residual Photocurrent at a Mercury Electrode. J. Electroanal. Chem., 62 (1975) 341.
76 with A.W. Gardner, An Electrochemical Temperature Perturbation Method using Modulated Light. J. Electroanal. Chem., 65 (1975) 95.
77 with D. McKeown, Modulation Polatography of DNA and some types of RNA. Preprint, 3rd International Symposium on Bioelectrochemistry, KFA, Jülich, Oct. 1975.
78 Large Signal Aperiodic Equivalent Electrical Circuits for Diffusion and Faradaic Impedances. J. Electroanal. Chem., 58 (1975) 5.
79 with G. Bottura and B. Bubani, Use of Homogeneous Competition for OH Radicals in Studies of H Abstraction from Organic Molecules. J. Electroanal. Chem., 62 (1975) 259.

Electrochemical Patents

British Patent 709826 (1954) — Square Wave Polarograph.
British Patent 820244 (1959) — Filter Circuit for Pulse Polarograph.
British Patent 870451 (1961) — Radio Frequency Polarograph.
British Patent Application P 36251/62 Electrochemical Transistors.
British Patent 1 287 100 (1972) with A.W. Gardner and A. Pope — Modulation Polarograph