Mousson in 1973, at Jülich in 1975, at Woods Hole (Mass.) in 1977, and at Weimar in 1979; the next one is being scheduled to be held in Israel in 1981 and the one after that, in England in 1983.

A journal and a series of publications especially devoted to bioelectrochemistry have been founded; the journal *'Bioelectrochemistry and Bioenergetics'* is in its 7th year of publication (now as a section of the *'Journal of Electroanalytical Chemistry'*[3] and 3 volumes of the series *'Topics in Bioelectrochemistry and Bioenergetics'*[4] have already been published, the 4th being in press and the 5th in preparation.

Furthermore, the international Bio-Electrochemical Society (BES) was founded to provide scientists interested in the phenomena with an active forum so that they could meet and discuss their problems[5].

This article appears without bibliographical references; for each one of the fields mentioned a very long list of references should be compiled. Readers interested in one or more of the subjects mentioned will find extensive bibliographic lists at the end of each article published in the volumes of the serial *'Topics in Bioelectrochemistry and Bioenergetics'*, which has just been written with the scope of a first pedagogical introduction to the different fields of bioelectrochemistry.

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[1] See J. electroanalyt. Chem. Interfacial Electrochem. *100*, 1 (1979).

[2] For this work Prof. Prigogine was awarded the Nobel prize for Chemistry in 1977.

[3] Elsevier Scientific Publishing Co. Amsterdam, Oxford, New York.

[4] John Wiley and Sons, Chichester, New York, Brisbane, Toronto.

[5] For information and application form write to the Secretary General, Prof. Dr. H.W. Nürnberg, Institut für Chemie IV Angewandte Physikalische Chemie, Kernforschungsanlage, D-517-Jülich, Federal Republic of Germany.

Historical roots of bioelectrochemistry

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The term 'bioelectrochemistry' was created at the 1st International Symposium Rome, 1971, although the first observations of galvanistic phenomena had already been described in the 18th century. In 1760 a Swiss physician, J.G. Sulzer (1720-1779) noticed that the combination of pieces of lead and silver caused a strange taste on his tongue, something like $FeSO_4$ solution. Connecting 2 different metals likewise with the nerves of frog legs, L. Galvani (1737-1798), anatomist at Bologna, discovered muscle convulsions in 1786. Some years before he had observed the same effects on frog legs, joined with one metal wire only, induced by an electrical machine or electrical discharges in the atmosphere. He published his results in a booklet with the title, 'de Viribus Electricitatis in Motu Musculari Commentarius' including 4 engravings of the experimental apparatus. He believed that muscles contained many little Leyden jars and produced electricity from inside, overlooking the prerequisite of the bimetallic connection. This explanation for the so-called 'animal electricity' might have been influenced by information from certain fish producing electricity, as discovered in 1774 by the physicist, J. Walsh (1725-1795). Therefore Galvani came to the false conclusion for the galvanic action, although his model fits fairly well with the electric organ of some fishes. This error of Galvani has been corrected by A. Volta (1745-1827), the famous physicist, who pointed out that the electricity comes from outside and the muscle works only as an indicator (electroscope), whereas nerves have the function of conductors. A prerequisite of galvanic action must be: 2 metals (conductors of the 1st class) and 1 electrolyte (conductor of the 2nd class). Despite his sophisticated experiments, especially with the voltaic battery, Volta's explanation for galvanism was erroneous, too. Volta postulated that electricity is produced only by the contact of both metals, in other words by a kind of perpetuum mobile[2]. Famous men, e.g. J.J. Berzelius (1779-1848), believed in this contact model, until in 1840 M. Faraday (1791-1867) finally refuted it[3]. Nevertheless, many people became excited by these phenomena between biological objects and electricity, and galvanism had an attraction comparable with that of molecular biology nowadays.

Quite another explanation was given by G.V.M. Fabbroni (1727-1822), an Italian chemist, in 1792, but published later[4]. He attributed galvanic actions, inclusive of taste sensitivity changes as in the case of the Sulzer experiment, to real chemical reactions without any generation of electricity present. However, the right interpretation[5-7] of galvanic action was presented by a 23-year-old student of Alma Mater Jenensis, Johann Wilhelm Ritter (1776-1810), who had worked in the field of galvanism since 1797, stimulated and encouraged by A. v. Humboldt (1769-1859), C.H. Pfaff (1773-1852), F.A.C. Gren (1760-1798) and others in Germany. First of all he found out the relationship between the contact potential series after Volta and the possibility of oxidizing these metals, as well as determining the sequence in which metals are able to precipitate each other out of their salts[5].

Therefore, he concluded that galvanism operates in the inorganic world too, and it is the universal key for the inner workings of nature[6]. Furthermore Ritter showed the chemical basis of galvanism[7] by the following simple experiment: he put a copper coin on a zinc slab and connected both by a drop of salt water. This little battery worked after a short circuit of Zn- and Cu-poles because the water became milky white as the zinc was oxidized. Ritter made a lot of similar experiments showing unambigously the chemical processes during galvanic action. Because Ritter explains galvanism in terms of chemistry, he is the founder of scientific electrochemistry[8-10]. In the case of living systems, J.W. Ritter believed that all organisms consist of many little galvanic batteries. He was able to show the parallelism in electrical stimulation between frogs and *Mimosa pudica* L.[11]. From sophisticated experiments, he derived the rule of polar excitation (later: Pflügersches Zuckungsgesetz) and the principle of accomodation, which act as prerequisites for the Weber-Fechner-rule. Besides these important results he described many new effects in stimulation-physiology especially on his own body[12]. The poles of a voltaic battery he put on his sense organs until he felt strong pain. For instance, a cathode wire placed in contact with his eye caused the impression of a blue light, which changed to red after circuit interruption. Vice versa are the effects for the anodic contact. Surveying his whole research field one must say that J.W. Ritter founded bioelectrochemistry, too. Besides these discoveries he detected UV-irradiation in 1801 and invented electrochemical instruments during his 8-year period at Jena[13-17]. This early electrophysiological work summarized by P. Sue[18] was developed further by E. du Bois-Reymond[19], physiologist (1816-1896), F. Hoppe-Seyler, physical chemist (1825-1895), and H. v. Helmholtz, physiologist and physicist (1821-1894), who measured the speed of nerve impulse and reflex processes.

Most important for the theoretical understanding of electrochemical forces in general were the dissociation theory[20] of S. Arrhenius, chemist (1859-1927), in 1887 and the Debye-Hückel-Theory[27] for strong electrolytes in 1923. In the first half of the 20th century, the biochemical redox processes and the proton exchange system became essential and were studied more and more by electrochemical techniques. Besides the propagation of irritation the mechanism of photosynthesis, respiration and cancer metabolism became the most interesting fields of research developed by O. Warburg, a German biochemist (1883-1970). In the past 20 years, bioelectrochemistry has been characterized as a rapidly growing branch of electrochemistry, working mainly with expensive techniques, polarography combined with spectrophotometric methods[22] as was demonstrated in 1965 at the Jena symposium[23]: Electrochemical Principles and Methods in Molecular Biology. Nowadays progress is discussed at the International Bioelectrochemical Symposium, started at Rome (1971), followed by Pont-à-Mousson (1973), Jülich (1975), Woods Hole (1977) Weimar (1979); all results are published in 'Bioelectrochemistry and Bioenergetics'[24]. New trends are now being distinguished, e.g. membrane transport, brain processes, bone healing and influences of electrical fields on all of these[25].

Table 1. Discoveries of J.W. Ritter during 1796-1804 at Jena

1797	Galvanic action has chemical source (electrochemistry)
1798	Qualitative anticipation of Weber-Fechners law (electrostimulation)
1800	Quantitative electrolysis of water
1801	UV-radiation in sunlight
1801	Light influence on electrode reactions (photo-electrochemistry)
1801	Mercury movement by polarization (electrocapillarity)
1802	Accumulator principle
1804	Current differences in branched wires (Kirchhoffs law)
1804	Electrochemical processes in all living beings (bioelectrochemistry)

Table 2. From galvanism to electrochemistry and its consolidation in the 19th century

J. Walsh	(1725-1795)	electric fishes
L. Galvani	(1737-1798)	galvanism = vis vitalis
G. Fabbroni	(1727-1822)	galvanism = chemical reaction
A. Volta	(1745-1827)	galvanism = contact potential
P. Erman	(1764-1851)	galvanism-friction electricity
Ch. Pfaff	(1773-1852)	teacher of galvanism
J.W. Ritter	(1776-1810)	**galvanism = electrochemistry**
J. Berzelius	(1779-1848)	electrolysis
C. Matteucci	(1811-1868)	electrode polarization
E. DuBois-Reymond	(1818-1896)	electrophysiology
F. Hoppe-Seyler	(1825-1895)	electrophysiology
H. v. Helmholtz	(1821-1894)	nerve excitation
S. Arrhenius	(1859-1927)	theory of ions
W. Ostwald	(1853-1932)	dissociation and conductance

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1 L. Galvani, De Bononiensi Scientiaricum et Artium Instituto atque Academia Commentarii, *VII*, 363 (1791).

2 A. Volta, Brugnatelli's Giurnale Fiscico-Medico, November (1792) S. 192.

3 M. Faraday, Phil. Trans. R. Soc. 61 (1840).

4 G.V.M. Fabbroni, Nicholsons Q. J. nat. Philosophy *3*, 308 (1799).

5 J.W. Ritter, Beweis, dass ein beständiger Galvanismus den Lebensprozess in dem Tierreich begleite. Nebst neueren Versuchen und Bemerkungen über den Galvanismus, V. Industrie-Comptoir Weimar 1798.

6 J.W. Ritter, Beweis, dass der Galvanismus auch in der anorganischen Natur zugegen sey. Vortrag Naturf. Ges. Jena, 1799.

7 J.W. Ritter, Beiträge zur nähern Kenntnis des Galvanismus und der Resultate seiner Untersuchung, 2 Bd. Jena 1800-1805.

8 W. Ostwald, Elektrochemie, ihre Geschichte und Lehre. Akad. V. Ges., Leipzig 1896.
9 H. Schimank, Johann Wilhelm Ritter, der Begründer der wissenschaftlichen Elektrochemie. Abh. Ber. dt.Mus. *5*, 175 (1933).
10 Worlds Who's Who in Science, p. 1428. Marquis, Chicago 1968.
11 J.W. Ritter, Denkschr. K. Akad. Wiss., München, *11*, 254 (1811).
12 J.W. Ritter, Gilberts Annln. Phys. *7*, 447 (1801).
13 Bibliographie Universelle, Paris, *B8*, 136 (1824).
14 Poggendorffs Annln. Naturwiss. Leipzig II 652 (1863).
15 A. Hermann, Die Begründung der Elektrochemie und Entdeckung der ultravioletten Strahlen. Akad. V. Ges. Frankfurt a.M. 1968.
16 H. Berg, Spektrum *12*, 32 (1976).
17 H. Berg und D. Germann, in: Der junge Schelling, p. 83. H. Böhlaus Nachf., Weimar 1977.
18 P. Sue, Histoire du Galvanisme et Analyse. Bernard, Paris 1802.
19 E. Du Bois-Reymond, Untersuchungen über tierische Elektrizität, Berlin 1848/49.
20 S. Arrhenius, Z. physik. Chem. *1*, 631 (1887).
21 E. Hückel, Ergebn. exakt. Naturw. *3*, 199 (1924).
22 Th. Shedlovsky, Proc. Symp. Electrochemistry in Biology and Medicine, New York 1953.
23 H. Berg, ed., Elektrochemische Prinzipien und Methoden in der Molekularbiologie. Akademie Verlag, Berlin 1966.
24 G. Milazzo, Ed, Rome. Vol. 1-5 Birkhäuser, Basel 1974-1978; from vol. 6, Elsevier, Holland.
25 1st Gordon Conf. Bioelectrochemistry, 1980. Ed. N.H. Tilton.

Electrode technique

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Introduction

The application of contemporary electrochemistry to the study of compounds and phenomena of biological significance is intimately connected with the role of specific electrode intervention in and response to such compounds and phenomena. Such application has ranged from the in vitro study of redox reactions involving small molecules occurring in biosystems to the in vivo study of the effects of the insertion of electrodes in damaged anatomical areas. Space allows only a cursory description of current lines of research involving the focal action of electrodes in bioelectrochemistry, which may itself be defined as the application of electrochemical principles, methodology and techniques in order to gain a better understanding of biologically relevant systems.

A recent development of great potential importance is that of modified electrodes to which biological compounds and species are attached for the purposes of better examining biological processes and of investigating electrochemical regeneration of the products of chemical and biochemical (e.g., enzymatic) reactions with respect to chemical processing and energy conversion.

With regard to electrodes, the commonly used potentiometric and voltammetric (including polarographic) techniques of measurement basically require an indicating or working electrode, which equilibrates with the chemical species of interest or engages in a faradaic process with it, and a reference electrode to which the potential developed at the indicating electrode or applied to the working electrode can be referred. If an appreciable current flow or IR drop is involved, a counter electrode can be advantageously added with the working and counter electrodes in the electrolysis loop while the working and reference electrodes are part of a potentiometric loop.

Electrode types

The *indicating electrodes* used in potentiometry may be zero class electrodes, which equilibrate with electron transfer-processes, e.g., platinum, graphite or mercury, or 1st class electrodes of metal which equilibrate with ions of that metal, e.g., a silver wire immersed in a Ag(I) solution. The latter type of electrode is readily converted in many cases to a 2nd or 3rd class electrode which, for example, responds to the activity of anions or cations which are involved in solubility or complex-formation equilibria with the 1st class electrode cation, e.g.,

2nd class electrode: La, LaF_3/F^-

3rd class electrode: Ag, Ag_2 S, CuS/Cu^{++}

Many selective ion electrodes are 2nd and 3rd class electrodes. Such potentiometric electrodes are well covered in the literature[1-3].

Reference electrodes, whose primary requirement is that their potential is not appreciably altered on modest current flow, are well described by Ives and Janz[4]. Potentials subsequently cited, unless otherwise noted, are referred to the aqueous saturated calomel electrode (SCE).

Counter or *auxiliary electrodes* are generally of platinum, less frequently of some other noble metal or graphite, and are usually used in the form of wire spirals, rods, gauze or solid sheets. The area must be sufficiently large that the complementary faradaic process occurring at the counter electrode does not become rate-limiting.

Subsequent discussion is focussed on the *working electrode* as the latter is used to examine processes