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ORIGINAL PAPER

From the Leiden jar to the discovery of the glass electrode by Max Cremer

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Abstract The discovery of the glass electrode by Max Cremer was possible because of the advances made in the nineteenth century in understanding the electrical properties of glass, and because of the studies of electrical potential drops at the interface of phases. The discovery of the Leiden jar by E. G. von Kleist and the follow-up studies of the properties of that capacitor disclosed that glass is a dielectric. Much later, the ionic conductivity of glass was noticed and studied by J. H. Buff, W. von Beetz, W. Thomson (Baron Kelvin of Largs), W. Giese, H. L. F. von Helmholtz, E. Warburg, etc. It needed also the discovery of electromotive forces due to the partition of mobile ions (charge separation) by W. Nernst and E. H. Riesenfeld to pave the way for the idea that ion partition also occurs at solid–solution interfaces producing electromotive forces (emf). At the beginning of the twentieth century, the ground was laid to expect that a very thin glass membrane may produce an electromotive force because the glass has a finite ionic conductivity and ion partition may cause an emf. It obviously needed a physiologist like Max Cremer who desired to mimic a cell membrane (a semipermeable membrane), to use a glass membrane for that purpose. Cremer's congenial choice of a thin glass bulb was rooted in a thorough understanding of the origin of electromotive forces, and it was not initiated directly by the Giese-Helmholtz cell, as some later reviews suggested. Later Cremer realized that an emf builds up when aqueous solutions are separated by a thin glass membrane. Cremer's discovery was picked up by F. Haber who developed the glass electrode together with his PhD student Z. Klemensiewicz as an analytical tool. The following decades have brought improvements of the glasses and measuring techniques, and a deeper insight into the functioning of the glass electrode. Here, it will be shown that full credit for the discovery of the glass electrode effect must be given to Max Cremer. Unfortunately, his role has not been adequately described so far, mainly because Haber dominated the literature.

Introduction

Glass electrodes are the most widely used pH sensors, and they are doubtlessly the most frequently used analytical electrodes in laboratories and in industry. The great success of glass electrodes is the result of the following properties: (1) glass electrodes have a very high selectivity for H_3O^+; (2) they are especially insensitive to changes of the redox potential of solutions, i.e., they are easily applicable in oxidizing and reducing solutions; (3) they are relatively cheap in production; (4) they can have a long lifetime, provided they are maintained properly. These advantages outweigh the disadvantages, which are: (a) they always need to be calibrated, (b) they are mechanically fragile, (c) they cannot resist HF-containing solutions, (d) they are not very well-suited for micro-applications, and (e) their application in food industry and for in vivo measurements in medicine is severely restricted. However, all in all, the development of glass electrodes is a story of great success, and it did not find an end yet. Although the early steps of

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The author dedicates this paper to Dr. F. G. K. Baucke as a sign of highest appreciation for his fundamental contributions to the understanding of the electrochemistry of glass electrodes, and as a personal thank-you for the support he has given to this journal since its start.

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development have been occasionally mentioned, and a number of monographs and book chapters have been written about glass electrodes [1–10] there is still no balanced description of the early history, and the role of Max Cremer did not find the necessary attention. The larger the time distance from the early steps in the development of glass electrodes, the larger are the distortions in the description of the history. This happens partially because some authors did not perform a sufficiently detailed historical search, partly because others omitted mentioning some of the involved persons, and then there are other authors who simply copied some of the distorted statements. In the history of science, one may find many examples for such distortions. In the case of glass electrodes, one can frequently find references to Fritz Haber, already less frequently to Fritz Haber and his Polish Ph.D. student Zygmunt Klemensiewicz, and only occasionally people refer to the work of Wilhelm Giese, the assistant of Hermann von Helmholtz, and to the important work of Max Cremer. In this paper, the attempt is to unravel the path of events and ideas, and to give a more detailed view of the role which Max Cremer played.

In the development of the glass electrode, the following periods can be distinguished:

1. At the beginning, we should take note of Stephen Gray's discovery of electrical conduction and electrical insulators, among which he also has used glass. Shortly later, experiments with electricity have been performed using glass vessels, the so-called Leiden jars, as storage devices for electricity (capacitors), and the different behavior of different glasses has been observed. The main players of that period were Ewald Jürgen (Georg) von Kleist, Pieter van Musschenbroek, Andreas Cunaeus, and Henry Cavendish.
2. In the next period, systematic studies of the electric conductivity of glasses have been performed at room temperature and at elevated temperatures, and it has been realized that glass is an ionic conductor and not only a dielectric medium. The main advances of that period were achieved by Buff, von Beetz, Thomson, Giese, and von Helmholtz.
3. The third period is a very short but revolutionary development of the idea to use a glass membrane to mimic physiological membranes and to understand the membrane as the locus of formation of an electromotive force (emf). It will be shown here that this revolution did not happen as a linear continuation of research on glass electrochemistry, and it was even not inspired by the previous findings; although the knowledge gathered in the previous two periods was certainly a prerequisite. This revolutionary development is the merit of the German physiologist Max Cremer.
4. The fourth period was the forceful development of the glass electrode and its characterization by Fritz Haber and his Polish PhD student Zygmunt Klemensiewicz.
5. The fifth period is characterized by the development of the most suitable glasses by MacInnes [11], and the introduction of vacuum tube amplifiers by Beckman [12] which greatly facilitated the measurements, and which finally led to the modern semiconductor-based pH meters in conjunction with combination electrodes. The fifth period is also characterized by a substantial development of the theory of glass electrodes, with prominent contributions from F. G. K. Baucke, to whom this special issue of the Journal of Solid State Electrochemistry is faithfully dedicated.

The first period (roughly from 1730 to 1770)

Following Stephen Gray's (1666–Feb., 15, 1736) discovery of electrical conduction and electrical insulators in 1729 [13, 14] the development of the Leiden jar was of exceptional importance for the understanding of the properties of glass. The early history of the Leiden jar has been described in detail by Christoph Heinrich Pfaff (1773–1852) in "Gehler's Physikalisches Wörterbuch" (physical dictionary) [15]: The Leyden jar has been discovered by Ewald Jürgen (Georg) von Kleist, dean of the chapter ("Dechant des Domkapitels") at Camin (Kammin), Pomerania, Germany (now Kamień Pomorski, Poland). E. J. von Kleist was born June 10, 1700 in Vietzow (now Wicewo, Poland) and died October 11, 1748 in Köslin (now Koszalin, Poland) [16]. He studied law in Leipzig and Leiden (a fact that is not connected with the later naming of the jar), was dean of the chapter in Camin from 1722 to 1744, and afterwards president of the Royal Court ("königliches Hofgericht") at Köslin. He was a member of the Academy in Berlin. E. J. von Kleist observed the possibility to store electricity in a jar on October 11th, 1745, and he reported this finding in letters to several people: (a) to Dr. Lieberkühn in Berlin on November 4th, who soon reported the discovery to the Academy in Berlin; (b) to the priest Swierlick (others give the name Swietlicki) in Danzig (now Gdańsk, Poland) on November 28th, who reported this to the "Danziger naturforschende Gesellschaft" (Danzig Society of Natural Scientists); (c) and finally to Professor Johann Gottlob Krüger (1715–1759) in Halle who communicated it in his book "Geschichte der Erde in den alleraltesten Zeiten" [17, 18]. In 1746, Pieter van Musschenbroek (March 14, 1692–September 19, 1761) reported from Leiden to René-Antoine Ferchault de Réaumur (1683–1757) an experiment with an electric jar, and the French started to call the experiment (the charging of a glass jar) as the "Leiden experiment". Jean Frédérique

François Louis Allamand (1736–1803), another Professor in Leiden reported in a letter to the French abbot Jean Antoine Nollet that the electric jar was discovered in Leiden by Andreas Cunaeus (1712–1788). Allmand reported the electric jar also in a letter to the Royal Society of February 4, 1746. Nollet translated that letter and published it in 1746 in the Mémoires [19]. Nollet called it the Leiden jar (in the past written Leyden jar), a name that was kept since, despite numerous pleas to call it the Kleist jar [20]. Figure 1 depicts a battery of Leiden jars.

What was the main gain in knowledge resulting from the development of and experiments with the Leiden jar with respect to electricity and glass? Certainly, it was realized that glass is a very effective electric insulator. Today this sounds very trivial, but at a time when the nature of electricity was completely unknown, when neither electrons nor ions were known, this was an important empirical finding. However, it also directed people to think of glass as being always an insulator.

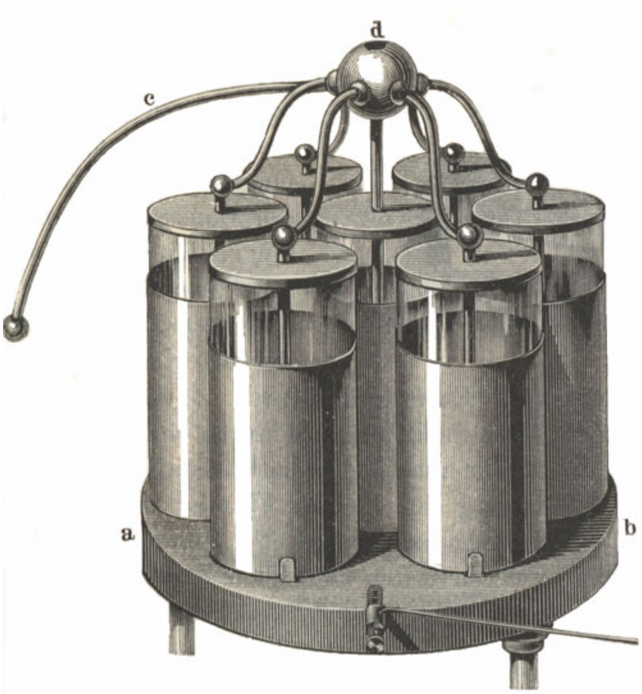

Fig. 1 Battery of Leiden jars: *a* and *b* is a wooden board with tinfoil on top. This wooden board sits on glass feet. *d* is a metal sphere which serves as connector to the smaller metal spheres on top of each jar. Each jar has a wooden cap, through which a metal cylinder connects the bottom of the jar with *d*. All jars are covered inside and outside with tinfoil. The metallic connector *c* serves to charge the inner tin foils of the jars with respect to the outer tin foils. The outer tin foils may be connected with earth with the help of a clamp attached to the metal cover of the wooden base *a*–*b* (reproduced from [21]. The figure has been slightly reworked electronically to improve the contrast)

The second period (roughly from 1770 to 1890)

Musschenbroek already reported that some sorts of glass are not suitable to produce Leiden jars, and it may be speculated that a too large conductivity was the reason. Henry Cavendish (1731–1810) observed that heated Leiden jars lose the ability to store electricity, and he was probably the first to look at the conductivity of glass at elevated temperature [22]. Johann Heinrich Buff (Figs. 2 and 3)

Fig. 2 Johann Heinrich Buff (Liebig Museum, Gießen). Johann Heinrich Buff (May 23, 1805, Rödelheim–December 24, 1878, Gießen; see also his biographies in [24–27]) was the son of the Dutch captain Wilhelm Karl Ludwig Buff and his spouse Elisabeth Charlotte Lamprecht. The aunt of J. H. Buff, i.e., his father's sister, Charlotte Buff (January 11, 1753–Jan. 16, 1828) was immortalized by Johann Wolfgang von Goethe in his "The Sorrows of Young Werther" ("Die Leiden des jungen Werther") where Charlotte Buff gave the model for the Lotte. Charlotte has visited Goethe in 1816 when she was already in her mid-sixties and mother of 12 children [28]. This encounter inspired Thomas Mann to write his famous novel "Lotte in Weimar" (the English title is "The beloved returns"). By his two marriages J. H. Buff became related to August Wilhelm von Hoffmann and Justus von Liebig. He had six children with his first wife Johannette, and five children with his second wife Johanna. J. H. Buff made his doctorate under the supervision of Justus von Liebig in Gießen, he worked with Joseph Louis Gay-Lussac in Paris, and later he was in Kassel at the same time when Robert Bunsen was there. J. H. Buff contributed to various fields of chemistry and physics. With Friedrich Wöhler, he performed a study on SiH_4 which paved the way for silane chemistry. J. H. Buff was professor of physics at the University of Gießen. In a textbook on physical and theoretical chemistry (1857) which was coauthored by H. Kopp and F. Zamminer, the field of Physical Chemistry was, for the first time, treated as a special topic [29]. Buff also wrote numerous entries (e.g., the entry "Galvanismus" [30]) of the famous "Handwörterbuch der reinen und angewandten Chemie" edited by Liebig, Poggendorff, and Wöhler

Fig. 3 Johann Heinrich Buff, Friedrich Wöhler, Herman Kopp, and Justus von Liebig playing whist (Liebig Museum, Gießen)

mentioned in 1854 [23] that since Cavendish's observation no studies of the conductivity of glass at higher temperatures have been performed. Buff confined the temperature to the range 40–230 °C, observing appreciable conductivities already at temperatures of 40–50 °C. His studies mark an important change in the perception of glass because that material was seen before as being only an insulator, and indeed as one of the best.

In the second half of the nineteenth century, some other prominent physicists have also studied glass conductivity: William Thomson (Baron Kelvin of Largs) [31], Wilhelm von Beetz [32], and Emil Warburg [33]. Thomson had shown that a galvanic cell consisting of two different metals separated by a flint glass plate produces an emf. Whereas Thomson and Warburg are very well known, much less has been written about Wilhelm von Beetz (Fig. 4). In his paper from 1854, Beetz [32] could show that glass is an electrolytic conductor below its melting point. He dissolved the two ends of a glass rod made of "Fuch's Wasserglas" [34] (water glass, liquid glass) that served before as conductor (below the melting point), and showed that the solution of the end which was in contact with the positive pole was not anymore alkaline, whereas the reaction of the other end was even stronger alkaline than before the experiment. He also performed experiments with "ordinary glass" and found an electrolytic conductivity.

Fig. 4 The founders of the "Physikalische Gesellschaft zu Berlin" in 1845, top row: G. Karsten, W. Heintz, C. H. Knoblauch; bottom row: E. Brücke, E. du Bois-Reymond, W. von Beetz. Wilhelm von Beetz was born March 27, 1822, in Berlin. Following his studies he became Privatdozent, later Professor at the cadet corps and the artillery and engineering school in Berlin. In 1855, he became Professor in Bern, in 1858 in Erlangen, and in 1868 in Munich (Technical Highschool). From 1874 to 1877 he was Director of the Polytechnic in Munich and in 1876 he was ennobled (personal nobility). W. von Beeetz died January 22, 1886, in Munich. Together with the physicists Gustav Karsten, Carl Hermann Knoblauch, Wilhelm Heintz, and the phsiologists Emil du Bois-Reymond, and Ernst von Brücke, he has founded the "Physikalische Gesellschaft zu Berlin" ("Physical Society at Berlin"), the forerunner of the "Deutsche Physikalische Gesellschaft" ("German Physical Society") on January 14, 1845

The next step in the history of the glass electrode was made by the physicist Wilhelm Giese (May 27, 1847, Colberg, Germany (now Kołobrzeg, Poland)–?). Giese studied at the University of Berlin from 1868–73, worked as teacher at the "Joachimstalsches Gymnasium" (Berlin) from 1875 to 1877, and was thereafter assistant of von Helmholtz at the physics institute of the university [35]. In 1880, Heinrich Hertz became the successor of W. Giese as assistant to von Helmholtz [36]. Surprisingly, Koenigsberger [49] does not mention Giese in his very comprehensive three-volume biography of von Helmholtz. From June 1882 to October 1883, Giese was the scientific leader and commander of a polar station in Kingua (Cumberland Sound, Baffin land) [37–39]. Since von Helmholtz was a member of the German Polar Commission, which met in 1881 in Berlin to prepare the German expeditions, and which appointed Giese as the scientific leader and commander of the Kingua Polar Station [37], it is highly probable that von Helmholtz has suggested his former assistant for that position. Giese has published his experiences in performing earth-magnetic measurements under polar conditions and he has given a number of suggestions for future undertakings of that kind [40, 41]. In a paper from 1889 [42], Giese mentions that since 1888, he has worked in his private laboratory, and before he has performed the experiments at the physics institute of the university. Giese has studied extensively the electric conduction through gasses and plasmas, and he arrived at the idea of gaseous ions being partly responsible for it [42, 43], which certainly must be seen as a result of his collaborative interaction with von Helmholtz [44]. Unfortunately, the author could not find a photo of Giese, neither could he find the details about his later fate and death. Giese was obviously an experimentally highly gifted physicist, who contributed to very different research fields, so that he is now known to polar scientists [38, 39], plasma scientists [36, 44, 45], and also electrochemists [1], but neither of these communities realized his whole scientific work.

In 1880, Wilhelm Giese published a paper in which he reported experimental studies on the origin of the so-called residues (“Rückstände”) in Leiden jars, i.e., on the origin of residual charges [46]. This paper is based on his PhD thesis published the same year [47]. From these experiments, he concluded that an electromotive force arises in the cell ‘tin–glass–sulfuric acid–platinum’. To exclude any solution film on the surface of glass, he has designed the cell as depicted in Fig. 5: an inner glass tube was filled with mercury (*Q*) which was contacted by the Pt wire d_1. The outer glass vessel contained an aqueous solution *S*. The entire glass cell was sealed by melting the parts together, and the inner part housing the mercury was evacuated to get rid of the last traces of water. This cell exhibited an electromotive force which was (1) depending on the composition of the aqueous solution, and (2) depending on the thickness of the glass layer separating the mercury and the solution, the electrometer was charged at a different rate (i.e., faster with thin glass). When Giese has filled the mercury into the tube *A*, he did not observe an emf because the cell was interrupted by the vacuum. Giese tried to measure the emf with the compensation method, but he obtained varying data for four kinds of glasses and at different dates (he reported results measured at Feb. 19, 1878, May 10, 1878, and May 17, 1879). The emf varied between 0.232 and 0.304 (in units of the normal element). One can take this as an early observation of the problems in using direct metal contacts for glass electrodes.

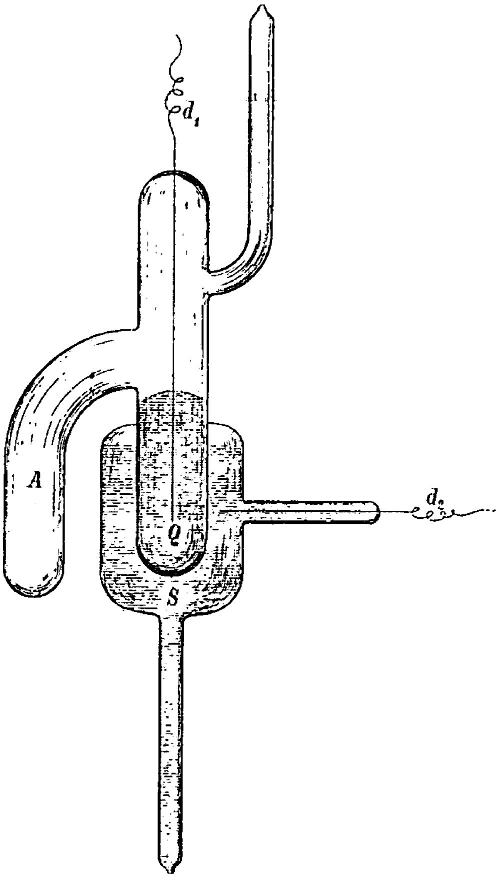

Fig. 5 Cell published by Giese in [46]: d_1 and d_2 are Pt wires, *Q* is mercury, *S* is an aqueous solution, *A* is an evacuated glass tube into which the mercury could be filled so that to interrupt the circuit d_1–*mercury–glass–solution*–d_2 (the figure has been slightly edited as to make *Q* and *S* better readable.)

One year after Giese published these results, on April 5, 1881, H. L. F. von Helmholtz (Fig. 6) gave his famous Faraday lecture in London, in which he pleaded for understanding electrochemistry in terms of charged particles: “If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity too, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity. As long as it moves about in the electrolytic liquid, each ion remains united with its electric equivalent or equivalents.” [48].

In this lecture, von Helmholtz also reports a cell which was, as he wrote, “constructed by my former assistant, Dr. Giese”. That cell (Fig. 7) deviates from the cell that Giese has already reported in 1880 in “Annalen der Physik” in the following point: the mercury was substituted by a copper solution in which a copper plated Pt wire dipped, and the outer cell compartment contained a zinc solution with zinc amalgam on the bottom which was contacted by another Pt wire. Hence, it was a Daniell cell with the glass (membrane) as separator. Helmholtz reported that the emf of that cell is practically identical with that of a conventional Daniell cell, and he did not dwell on the origin of the emf (perhaps because Giese had reported it already), but he emphasized that the experiments prove the finite conductivity of glass! He discusses the results as follows: “The

Fig. 6 Hermann Ludwig Ferdinand von Helmholtz (reproduced from [49]). Helmholtz (Aug. 31, 1821, Potsdam, Germany–Sep. 8, 1894, Berlin, Germany) is such a well-known physicist that it would be impossible here to give more details than are already easily available elsewhere [49–51]

whole charges the electrometer exactly like a Daniell's cell of very great resistance, and this it would not do if the septum of glass did not behave like an electrolyte: for a metallic conductor would completely destroy the action of the cell by its polarisation. All these facts show that electrolytic conduction is not at all limited to solutions of acids or salts. It will, however, be rather a difficult problem to find out how far the electrolytic conduction is extended, and I am not yet prepared to give a positive answer. What I intended to remind you of was only that the faculty to be decomposed by electric motion is not necessarily connected with a small resistance to the current. It is easier for us to study the cases of small resistance, but the illustration which they give us about the connection of electric and chemical force is not at all limited to the acid and saline solutions usually employed." From our modern perspective, one is tempted to assume that the experiments reported by Giese and von Helmholtz should have paved the way for constructing glass electrodes as tools for measuring solution properties. Especially following the introduction of the idea of ionic dissociation by Svante August Arrhenius (1859–1927) in 1884 in his PhD thesis, this would have been feasible. But history shows that about 25 years elapsed until Max Cremer made the next crucial step.

The third period (1906)

Since Max Cremer (Fig. 8) has published his seminal paper in 1906, one may suppose that he has performed the crucial experiments in the months before. Hence, that short period of discovery of the glass electrode effect may be simply dated to 1906.

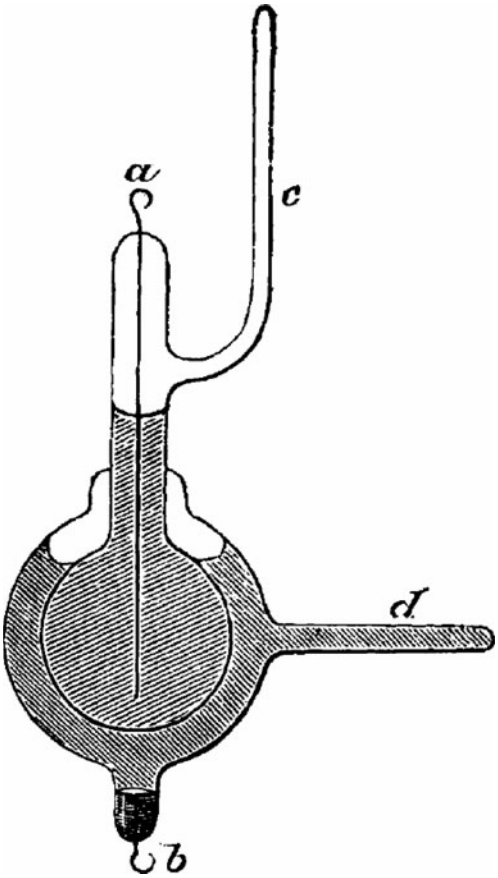

Fig. 7 Giese-Helmholtz cell. Helmholtz describes the cell as follows: "I show you, therefore, this little Daniell's cell, … , constructed by my former assistant, Dr. Giese, in which a solution of sulphate of copper with a platinum wire, *a*, as an electrode, is enclosed in a bulb of glass hermetically sealed. This is surrounded by a second cavity, sealed in the same way, which contains a solution of zinc sulphate and some amalgam of zinc, to which a second platinum wire, *b*, enters through the glass. The tubes *c* and *d* have served to introduce the liquids, and have been sealed afterwards. It is, therefore, like a Daniell's cell, in which the porous septum has been replaced by a thin stratum of glass. Externally, all is symmetrical at the two poles; there is nothing in contact with the air but a closed surface of glass, through which two wires of platinum penetrate. The whole charges the electrometer exactly like a Daniell's cell of very great resistance, and this it would not do if the septum of glass did not behave like an electrolyte: for a metallic conductor would completely destroy the action of the cell by its polarisation." [48]

Max Cremer was a pupil and co-worker of Carl von Voit (Oct. 31, 1831, Amberg, Germany–Jan. 31, 1908, Munich, Germany), one of the founders of modern nutrition science, and he followed his teacher in being seriously interested in the physiology of nutrition. In that respect, Cremer wanted to get a deeper insight into the function of biological membranes, and coming from that side of biochemistry, he attempted to study biological membranes both experimentally and theoretically. For this to achieve, he was very well trained after his

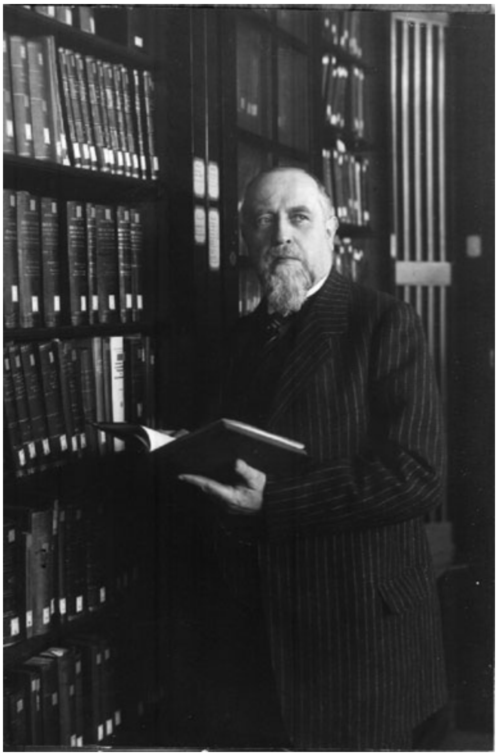

Fig. 8 Max Cremer, probably in 1925. That photo has been published in a Festschrift issue of Biochemische Zeitschrift [52], however the photo was only included in the personal copy for Max Cremer. This photo has been provided by Th. Cremer, Munich, grandson of Max Cremer. Max Cremer was born on March 11, 1865 in Ürdingen (now part of the town Krefeld), Germany. Cremer studied medicine at the Universities of Bonn, Würzburg, and Munich. He became a medical doctor in 1887 and the approbation as medical doctor in 1888. Following this he studied 8 semesters' mathematics and natural sciences because he wanted to become a physiologist. In 1890 he joined the physiological institute in Munich, habilitated in 1893, and became extraordinary Professor in 1901. From 1909 to 1911 he was director of the physiological institute of Cologne and professor at the academy of practical medicine of that city. From 1911 to 1933 he was director of the physiological institute of the then "Tierärztliche Hochschule" (veterinary high school) Berlin [53, 54]. Max Cremer's three children became well-known Professors: Erika Cremer [55] was a pioneer of adsorption gas chromatography, Lothar Cremer was an electro-technician (acoustics), and Hubert Cremer, a mathematician. Among his grandchildren are four professors. Max Cremer died May 22, 1935 in Munich

medical and science studies. The idea to use a very thin membrane of a solid material, e.g., glass, to produce an electromotive force across the membrane was obviously an original inspiration and it was not directly rooted in or prompted by the Helmholtz/Giese work discussed above. Max Cremer explicitly argues against that presentation (which was given in Freundlich's famous book "Kapillarchemie" [56]) of the cause of developments in his comprehensive chapter entitled "Ursache der elektrischen Erscheinungen" ("Reasons of electrical actions") in "Handbuch der normalen und pathologische Physiologie" ("Handbook of normal and pathologic physiology") in 1928 [57]. In 1906 Max Cremer published a paper entitled "Über die Ursachen der elektromotorischen Eigenschaften der Gewebe, zugleich ein Beitrag zur Lehre von den polyphasischen Elektrolytketten" ("On the reasons of the electromotive properties of tissues; at the same time a contribution to the doctrine of polyphasic electrolyte chains") in "Zeitschrift für Biologie" [58]. Cremer refers to an earlier publication in "Sitzungsberichte der Gesellschaft für Morphologie und Physiologie zu München" in 1900 [59] where he had already claimed that the electromotive forces of nerves can, in principle, be explained by knowing the concentration and properties ("Beschaffenheit") of the charged ions. In his paper from 1906 [58], Cremer explains what he understands as the relevant properties ("Beschaffenheit"): first, that are the "Wanderungsgeschwindigkeiten", we would say the diffusion coefficients of ions in (normally but not necessarily liquid) phases, and, second, that are the "Teilungskoefficienten", we would say partition coefficients of ions between phases. Electrochemical cells in which the electromotive force is caused by different diffusion coefficients only, Cremer calls "monophasische Ketten". We would speak about cells with diffusion potentials. When the partition of ions between different phases is the cause of an electromotive force, Cremer called the cell a "polyphasische Kette". The modern term would be cells with "distribution potentials". Of course, he uses especially the term "diphasisch" to specify the situation at one liquid|liquid interface. Cremer did also know the work of W. Nernst and E. Riesenfeld on the potential drop at liquid|liquid interfaces (he cites the PhD thesis of Riesenfeld [60] but here, the better accessible journal papers will be refrerred to as well: [61, 62]), which marked an essential step in the understanding of interfacial potentials due to partition. In the review entitled "Ursache der elektrischen Erscheinungen" ("Reasons of electrical actions") [57] Cremer discussed a paper of R. Luther [63] in which that author explains from a strictly thermodynamic point of view, that in a galvanic cell consisting of two metal electrodes (e.g., zinc) dipping in two different solvents, e.g., ether and water, containing a zinc salt, the potential difference between the two (equal) electrodes must be zero for the case that the partition equilibrium of the salt between the two solvents has been established: Zn|Zn-salt in ether||Zn-salt in water|Zn. It is interesting to see that Cremer attempted to prove this in a number of experiments with different metals, metal salts and also with Pt|dissolved iodine, and with hydrogen electrodes. Only in the case of copper electrodes and Pt electrodes in iodine solutions did he obtain almost negligible potential differences. For a physiologist, such experiments are very remarkable because they really touch very fundamental electrochemistry. This example shows that Cremer possessed the ability to follow the developments in theoretical electrochemistry, and tried to test the theory in well-designed experiments.

Cremer writes [57] in relation to Helmholtz's Faraday lecture "The idea that the glass as a diaphragm between the two liquids may possibly lead to a rather considerable electromotive force, obviously did not occur at that occasion to Helmholtz, and in any case no experiments have been arranged to test such possibility" (translated by FS). Cremer continues as follows: "I had the correct guess that, if one could somehow make very thin membranes of solid, badly conducting material, they possibly could give noticeable electromotive force in relative simple cells. For that membrane not to have cracks it should consist of a relative rigid material, in that connection I recalled the bulbs which the glassblowers used to fabricate when they join glass tubes; therefore I decided to perform experiments with such glass bulbs. Only later I carefully searched the literature in how far glass membranes have been used earlier for similar purposes. As it appears, that afterwards made careful description of the literature has been wrongly interpreted." (translated by FS). From this, it is clear that Cremer started his experiments with glass bulbs based on a very detailed knowledge about the origin of electromotive forces at interfaces. This simply makes him the real originator of the glass electrode. Cremer's review [57], published in 1928, had the primary goal to discuss the different theories explaining the origin of electromotive forces in physiological systems, namely (1) diffusion potentials (potential drops that arise due to different diffusion coefficients of anions and cations in one phase), (2) partition potentials (potential drops that arise at liquid|liquid interfaces due to the partition of ions), (3) concentration cells (potential drops between two reversible electrodes in solutions of different ion activity), (4) Donnan potentials (potential drops across a semipermeable membrane). Of course, at that time, it was impossible for Cremer to come to a final conclusion, as the structure of physiological membranes, especially ion gates, were not yet known. The review also mirrors a very fundamental problem: thermodynamics cannot tell anything about the mechanism, and correct thermodynamic calculations are often possible when assuming very different mechanisms. Thus, the theory applied by Haber and Klemensiewicz [64] assuming hydrogen electrodes on either side of the glass membrane leads to the same formally correct result as a description by partition potentials, since there are equilibrium constants allowing an interconversion of the data. Haber and Klemensiewicz as well as Cremer have been aware of that problem, although they did not explicitly discuss it. A second goal which Cremer obviously followed in writing the review [57] was to stress his priority claim for the glass electrode. From today's perspective, there can be no doubt that Cremer made the pivotal step in the development of that most important scientific instrument.

The fourth period and fifth period (from 1909 to the present)

At the time when Cremer published his paper in "Zeitschrift für Biologie" Fritz Haber (Fig. 9) has studied electrochemical cells with solid electrolytes, mainly heated polycrystalline salts [65]. Thus, Haber was obviously very well prepared to understand the glass electrode, at least from the point of ionic conductivity. Together with his Polish PhD student, Zygmunt Klemensiewicz (Fig. 9), he performed a very detailed study of the properties of glass electrodes which he published in 1909 [64]. The period following the

Fig. 9 Fritz Haber (*first row, sitting in the middle*) and Zygmunt Klemensiewicz (*second row, fourth person from right*). The photo shows Haber's research group in Karlsruhe in 1909. Reproduced with permission of "Archiv zur Geschichte der Max-Planck-Gesellschaft, Berlin-Dahlem"

work of Haber and Klemensiewicz is the time of maturing of the glass electrode as an analytical instrument, and also as a subject to study interfacial phenomena at solid|liquid interfaces where both phases possess electrolytic conductivity. The developments of that period will be treated in detail by other authors of this special issue.

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