

Hans Wenking, born August 18th, 1923
A Problem - Solver for Electrochemists

One of the centres of electrochemistry after the second world war was Goettingen, for a certain period perhaps the most productive one. Karl Friedrich Bonhoeffer and Eigen, Gerischer, Heusler, Kaesche, Vetter, Weil, ...the list of names remains incomplete. They laid the fundamentals of electrochemical kinetics, investigated the laws which describe the corrosion of metals.

Whether a certain material is stable in a certain environment, is described by electrochemical thermodynamics. Besides common parameters like pressure, temperature and ion activities, the electrical potential of a surface determines the region of stability for any material in its environment. It was Marcel Pourbaix who had collected an atlas which, in a very comprehensive manner, is used to determine where a material is stable, and moreover, which chemical composition will result out of the metal corrosion process. However, it cannot answer the question, at which rate such a process will proceed.

The relationship between the current passing an electrode and its potential was predicted by W. Nernst and could be determined with the help of simple systems at quite an early stage. If a constant current is passed through an electrode the resulting electrode potential can be measured. This was the method used to investigate thermodynamics. Using such methods, Julius Tafel was able to complete his works on "Hydrogen Overvoltage" on different metals hundred years ago¹. However, the range of the current in such an experimental set-up is restricted, a fact well demonstrated in Tafel's basic article. The mechanism of hydrogen evolution on metal surfaces was so far clarified (it was accomplished later by Volmer in 1930), yet the mechanisms of metal dissolution remained fairly unknown. The main problem in many instances was the hysteresis of the current - potential curve shown by many metals. A few electrochemists interpreted this as "passivity" of metals which Michael Faraday had already observed on iron in nitric acid. The recommended method now was to control the potential as determining variable instead of the current. The earliest attempts to control the potential were made in the thirties. Bruce and Hickling² described such an instrument in 1937, Hickling³ introducing the name "potentiostat" in 1942. Those early instruments were restricted to one polarity, the current ranges were limited, amplification was rather low (therefore the resulting potential error high), and stable operation was a permanent problem.

For a wide range of metals, the current-potential-curves remained incomplete: White spots on the electrochemical map, potential regions where the behaviour of the electrode remained unknown, where either heavy oscillations or unexplained hysteresis could not reveal the true action of the electrode.

Anyone looking at the current-potential-curve of a passivating metal sees the reason for these experimental difficulties at once. The curve is only *unequivocal* only if the potential is controlled to the desired value, and the current follows as dependent variable. As soon as e.g. an anodic current, which usually increases with increasing potential passes a peak and starts to decrease with increasing potential, a hysteresis will be shown in the galvanostatic curve. Early potentiostatic measurements, on the other hand, showed heavy oscillations in that potential range: Even if the potential could be controlled (in a way...), the results did not clarify

¹ J. Tafel, Z. phys. Chem. 50, 641, 1902

² Bruce, Hickling: J Scientific Instruments 14, 367, (1937)

³ Trans. Faraday Soc., 28, 27, (1942)

anything. Bonhoeffer and Eigen compared these oscillations to potential oscillations in nerves (an over-interpretation).

Staubach, electronic engineer with the Max Planck Institute for Physical Chemistry in Goettingen described the principal difficulties of a potential controlling amplifier by its internal phase shift and concluded, that such an instrument had to be adapted individually to the requirements of the individual electrochemical system. (We will not blame him: his main interest was in another field: he constructed - before De Maeyer - the high-voltage instruments which Eigen used for his famous works on "immeasurable fast reactions": nobel prize worth instruments, those!)

The question, why chromium alloyed steels do not rust remained without answer. Still less answered were the questions on the local breakdown of passive layers, leading to undesired corrosion effects like pitting.

Bonhoeffer's scientists struggled with such instruments. At last, Bonhoeffer assigned Hans Wenking, who had joined the institute just a year before with the construction of a new potentiostat. Whether he was conscious to have met just one of the few physicists who were capable at that time to solve such a problem, must be left undecided. At any rate, Wenking had already in 1952 designed a bulb amplifier which was used to control a mechanically recording amplitude - controlled oscilloscope⁴, operating in both polarities. At a later time, this amplifier was extended with a power stage to drive amplitude-controlled oscillating boards for biological applications. This oscilloscope - amplifier may be called the ancestor of modern semiconductor based operation amplifiers, showing all the features one finds in the principles of e.g. the well known TL 071 (Texas Instruments), or comparable types. The features were: differential input with an inverting and a non - inverting input, difference - forming in the next stage, high amplification (100 000) using constant current stages, dynamic feed - back. This amplifier was used as the core of the novel potentiostat, only a power stage had to be added.

Every amplifier shifts the phase of the input signal. The phase angle is a function of frequency, increasing with rising frequency. This does not influence a straight - forward amplifier. However, in a control amplifier where the signal from the controlled load is fed back into the control loop to obtain stable operation, the phase shift must never reach 180°. If it does, the feedback signal does not counterbalance the amplification, but increases it: This is the feature of an oscillator, much undesired for control operation.

A potentiostat is a control amplifier which, besides its own phase shift, has to control the current passing a cell. The electrode system within the cell forms a low pass filter, which itself introduces an unknown phase shift - any angle between near zero and 90° - into the control loop. Therefore, the allowed maximum phase shift of a potentiostat is 90°. This problem was to be solved. Early potentiostat manufacturers neglected this problem. The consequence were "singularities" during the experiment where the potentiostat started to oscillate. Sets of filters were used to damp the oscillations; filters, which had to be switched during the experiments when critical points were reached.

⁴ "Schleifenoszilloskop": A mirror - galvanometer was used to record fast oscillations up to some 100 Hz. The light beam recorded on photographic paper.

The solution for the problem was quite simple, in principle. The method is called "over - all - compensation" of the phase shift. By this method, the phase angle remains below 90° until the frequency - gain product is unity or less, i.e. the point where the amplifier damps and does not longer amplify. To follow electrochemical reactions, this critical frequency shall be higher than typical changes within the cell. Otherwise, the cell itself may start to operate in an undesired manner.

This were the features of the first electronic potentiostat designed by Wenking. Some other principles can be found in his instrument. Former potentiostats (Staubach) fixed the counter electrode to ground, and the signals of both working electrode and reference electrode floated with respect to the ground. Wenking fixed the working electrode to ground, and the potentiostat was operated like an operational amplifier today. His first potentiostats showed practically the principles of a present operation amplifier: differential input as the first stage, difference forming in the next stage, followed by a high-gain stage and a power stage. The features were high amplification, high common - mode rejection and internal dynamic feedback.

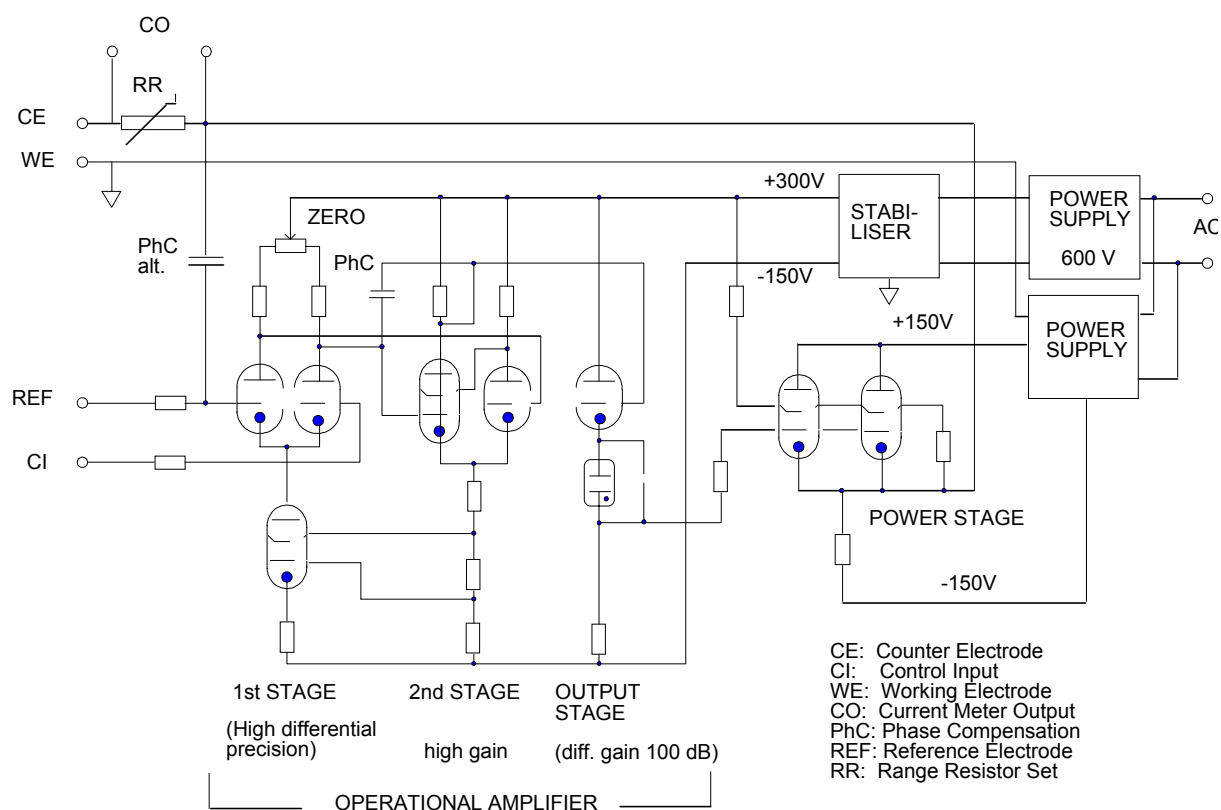


Fig. 1: Principle of an early Wenking - potentiostat

The results were discussed at the CITCE meeting in Stuttgart 1955, as a discussion, not a paper. The practical results had in the meantime confirmed the correctness of Wenking's design.

Until 1957 Wenking's potentiostats were only manufactured for the Max Planck Institute in Göttingen. In this period, Mr. Gerhard Bank, apprentice, and later craft with the MPI, was introduced in potentiostat manufacturing. His master piece, of course, was a potentiostat. The

publishing of the scientific results which were obtained with these instruments led to an increased demand. Mr. Bank could not stay with the MPI, in consequence Messrs. Wenking and Bank founded the "Elektronische Werkstatt Goettingen" to commercialise the potentiostats. From 1959, the potentiostat laboratory operated under the company name "Gerhard Bank Elektronik". Wenking designed the instruments as free lance but the brand "Wenking potentiostat" soon became a famous trade mark.

The consequence of the potentiostat development was a rush in the development of electrochemical science. The phenomena of metal passivity could better be explained, mechanisms of layer formation, and far beyond the materials science, the potentiostat became a standard instrument for most electrochemical investigations.

In addition, Wenking trained Mr. Alfred Jaissle, at this time craft with Gerischer at the Max Planck Institute fuer Metallforschung in Stuttgart. Also Jaissles Name is familiar in electrochemical and material science circles. Independent of Wenking's works, similar instruments were designed abroad. Tacussel was one of those who came to similar conclusions as Wenking (probably slightly later), and started his manufacture in France. In the USA however, Wenking's potentiostats were leading on the market. This and Wenking's habit of using English as language in his manuals led to the misunderstanding, that both the company Bank and Wenking himself were American.

Wenking has never published a line in scientific papers. Rare hints on his theoretical works are found as citations "unpublished", e.g. by Klaus J. Vetter⁵. On the other hand, Wenking never concealed the technical details of his instruments, (all) circuits and layouts were included in the operation manuals for the instruments, and even in some manuals, a detailed theoretical treatise was given (pages which probably never fascinated a chemist or materials scientist). The timidity to publish his works may be one of the reasons why, until today, publications on potentiostats can be found which do not meet the criterion of absolute stability.

For Wenking, the potentiostats were not a primary source of income, but a welcome add-on. He felt as a physicist, his foremost aim had always been to solve measurement and control problems. He solved different great problems, amongst others the realisation of an automatic operating ellipsometer. He did not like to be captured by institutions or companies, he liked to remain free lance, to be free to choose his tasks. This love for freedom is documented by his biography: in 1963 he joined the Max Planck Institute for Biocybernetics in Tuebingen, not as an employee, but as a consultant. There, he constructed instruments to investigate the optosensorics of insects. At the same time, he was working part-time with Zeiss in Goettingen. His optical instruments were never commercialised, however, the US Navy bought his patent for an instrument to measure the precise speed relative to the ground of aircraft by analogue correlation of the signals of two photosensors.

Nevertheless, Wenking was further interested in potentiostats. In 1961, he received a revolutionary part from an American scientist: A field effect transistor (FET). This FET was the first solid state transistor which reached the qualities of a bulb with respect to low input current and high input impedance. These FETs were instantly used to design the next generation of operational amplifiers: In his circuit diagrams, these are referred to as "BOP" or "FOV". These are discretely soldered amplifiers which were superior to commercial products

⁵ Klaus J. Vetter, "Electrochemical Kinetics", New York, London 1967

at that time. The first integrated operational amplifiers which reached the quality of those discretely soldered ones was the CA 081, which was introduced in Wenking's instruments in the late seventies.

Further works on potentiostats were undertaken by Wenking's to make the instruments faster: Higher slew rates, higher bandwidth to obtain most precise square wave - response. Furthermore, the method of current measurement was improved.

The early potentiostats had a set of current sensing resistors in the counter electrode circuit, the voltage across the range resistor is proportional to the current. This type of current measurement allowed a simple design of the potentiostat, and, moreover, neither bandwidth nor dynamics were affected. However, this voltage was not referred to ground, therefore any recording required chart recorders having a "floating" input. However, a ground - referred signal is easier to handle, and potentiostat - manufacturers tried to solve this problem in different ways.

There are different ways to obtain such a ground - referred current signal.

You may, for example, put the current sensing resistors in series between working electrode and ground. In that case, the voltage across this resistor, caused by a current, is added to the potential between reference electrode and working electrode: You have to form the difference between reference electrode voltage and the voltage drop across the current resistor to obtain correct potentials and correct currents. No problem, in fact, but it affects the "true" values a little bit: it decreases the precision of the signal and the bandwidth, and increases the noise. Beside the noise, the current signal suffers from the usual 50 Hz (or 60 Hz) power line hum because the working electrode is then no longer grounded, and the working electrode has to be shielded, too.

You may, for example, replace this "passive shunt resistors" with an active current sink, that is a zero -- ohm amperemeter. Now, the working electrode is kept on ground potential, and the voltage between working electrode and reference electrode input is nearly the true potential of the working electrode. Nearly, because a very small error remains, due to the fact that the gain of the current sink is not infinite and therefore introduces some deviation: less than 10^{-5} of the actual potential. However, the working electrode is not really grounded, it is kept on virtual ground and therefore prone to noise pickup and must be shielded. On the other hand: Only this concept allows the measurement of currents down to the picoampere-range, and below. One remark on low current measurements: The lowest range is defined by physical limitations. Whoever had the chance to repeat Millikans most famous experiment as a student knows: The electron charge is 1.6×10^{-19} Ampere-seconds: As soon as we start to measure femtoamperes, we have to count some thousand electrons per second. Latest in this range, an amperemeter becomes an integrator counting single electrons. And from the same experiment, we learn that the word "insulator" is somehow relative, there is no better insulator than a vacuum. Now, please, reflect the properties of a cable connection between your electrodes and the potentiostat.... In other words: The semiconductors known today do not reach the limitations, but are quite close to them. Any improvement coming is a factor of two, perhaps five, rarely ten. Then we reach limits as merciless as the absolute zero-point of the temperature-scale.

Others pleaded for the concept of "grounded counter electrode" - a method which seems attractive as long as the working electrode is enclosed in an autoclave. It is possible to design

such a potentiostat, however, in that case, you will earn all problems together: both reference electrode input and counter electrode input are floating, you are not allowed to exceed a certain voltage between counter electrode (now grounded!) and the working electrode - this limits the application of low-conducting electrolytes.

Wenking's idea was, to separate the internal ground of the power stage from the "signal" ground which was the grounding point of the working electrode. Doing so, and by introducing the current - to voltage - converting resistor between these two grounds, the current through the working electrode is forced to pass this resistor. As a consequence, he obtained the current - proportional voltage ground - referred, without lack of bandwidth. Especially for high current, high - voltage power potentiostats this principle is still superior.

The main problem of the current measurement is: As soon as you convert the potentiostat to a galvanostat, where the measured current is the loop - signal to control the instrument, any noise across the measurement resistor is amplified, and phase shifts caused by the current measurement which cause a phase shift near 180° will convert the potentiostat to an oscillator.

Wenking tried nearly all concepts, and the best were introduced for commercial models. His critical view to the works of others as well as to his own designs was sometimes extreme, this led at times to some mistrust in the capabilities of his customers. Otherwise it is difficult to imagine that he refused to offer potentiostats having extreme low current resolution. "Of course I can both measure and control currents in the order of picoamperes, but you will never be able to do so when a real electrochemical cell is connected" , he told me once when I asked for a potentiostat for low currents. A wrong estimation, as we know today.

Wenking's name has been established in electrochemistry, as far as analogue techniques were used. Grudging he implied digital techniques. His world was the world of analogue electronics. This was the world he ruled in a superior way, played virtuously on the keys, produced analogue processors, developed other instruments for electrochemists: integrators, scan generators, which produced true linear scans down to a few millivolts per hour. Where others used electromechanically driven scan generators, he designed pure analogue electronics. Before the first sample-and-hold amplifier was used to improve analogue-to-digital conversion, he had designed and used the predecessor in his automatically operating polarisation resistance meter.

In the meantime, electrochemical techniques proceeded to other topics. Stationary measurements, formerly performed as square-wave-pulses, were displaced by impedance measurements, strongly promoted by Göhr⁶. Electrochemical noise, first described by Tyagai⁷ more than twenty years ago, became one of the favorite methods now: It is the only method which does not influence the measurement itself by externally introduced polarisation. For all these instruments, potentiostats form the technical core. Prognosis: Fully digitally operating audio amplifiers are just starting to displace analogue stereo amplifiers. In the world of control amplifiers for electrochemistry, they are far from the requirements with respect to frequency limits and phase stability: some years will pass by before these techniques will offer adequate solutions.

⁶ H. Göhr, Ber. Bunsenges. Phys. Chem. 85, 264 (1981)

⁷ V. A. Tyagai, Electrochimica Acta 16, 1647, (1971)

Wenking is now 75 years old. His agility is unbroken. As soon as he learned, that electrochemical noise might bear process information, he started to improve low-noise amplifiers and filters. I am most grateful for his contributions, I inherited a mass of letters he wrote, explaining his tricky schematics, how to reduce the number of parts to an absolute minimum and thereby improving the quality.

Powerful potentiostats are in a way exotic instruments, electronic primadonnas which blame the designer for any careless treatment. Everybody who has basic knowledge of analogue electronics is able to make a small potentiostat. Whoever tried to upgrade such a small instrument to a power amplifier knows what I am talking about. Wenking could handle these primadonnas - no wonder, he was their progenitor.

"Ich habe einen Frack, der sitzt, einen Potentiostaten, der geht und ein Pferd, das läuft."⁸

This sentence, ascribed to Konrad Weil, shows best the value of Wenking's works for electrochemists.

⁸ "I have a dress - coat that fits, a horse that runs and a potentiostat that works."