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Impact of Kiukkola-Wagner Paper on the Development of Electrochemical Probes and Tools for Fundamental Studies and Industrial Applications

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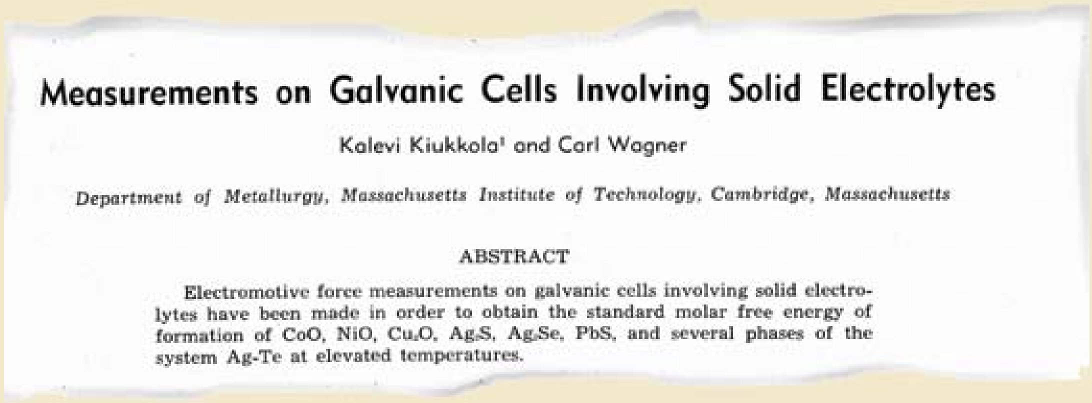
The 1957 paper, "Measurements on Galvanic Cells Involving Solid Electrolytes" by Kiukkola and Wagner[1] is just one example of the many fundamental scientific contributions made by Carl Wagner. Although Wagner is known for such fundamental contributions, he had, in fact, always looked at practical problems and needs.[2] This practical interest is apparent in his early work on corrosion,[3] which was, and continues to be, an important technological problem. In the same way, Kiukkola and Wagner's paper marks not only the beginnings of the era of the science of fast ionic transport in solids, but also the technology of ionics.

FROM: Carl Wagner and Kalevi Kiukkola, "EMF Measurements on Galvanic Cells with Solid Electrolytes" JES, **104**, 379 (1957).



Measurements on Galvanic Cells Involving Solid Electrolytes

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ABSTRACT

Electromotive force measurements on galvanic cells involving solid electrolytes have been made in order to obtain the standard molar free energy of formation of CoO, NiO, Cu_2O, Ag_2S, Ag_2Se, PbS, and several phases of the system Ag-Te at elevated temperatures.

Although Walther Nernst had demonstrated in the 1890s that various zirconia based oxides are "electrical conductors of 2nd class" (as ionic conductors were called at that time), it was not until a half century later that Carl Wagner concluded in a 1943 "Gedenkband" memorizing the death of Walther Nernst that doped zirconia conducts exclusively the large oxide ions by a vacancy mechanism. In spite of already mentioning at that time the application of this material in galvanic fuel cells, it was not until 14 years later, after post-war internment in the U.S. and moving to MIT (Cambridge, MA), that Carl Wagner in the Kiukkola and Wagner paper initiated the application of solid electrolytes in galvanic cells for practical applications. Carl Wagner realized the opportunity of electrochemical measurements at high temperatures, where equilibria among solid state materials are more readily established and therefore measurable. After examining various mixtures of oxides of thorium, lanthanum, and calcium, all of which showed a dependence of the electrical conductivity on the oxygen partial pressure indicating predominant electronic conduction, he eventually successfully employed 0.85 ZrO_2 + 0.15 CaO, which is still being used with minor variations in the kind and amount of dopant, as an electrolyte in solid oxide fuel cells (SOFCs) and sensors. This work provided the basis for fundamental studies and practical applications using solid electrolytes. A complete review of the impact of the Kiukkola and Wagner paper is far beyond the scope of this article, so just a few examples are provided for illustration purposes.

Impact on Fundamental Scientific Understanding

Thermodynamic measurements.—Kiukkola and Wagner demonstrated the use of stabilized zirconia in galvanic cells for measuring the standard Gibbs energy change for the formation of several oxides, including CoO by the following reaction.

$$\mathrm{Fe, Fe_xO}\left(\text{wüstite}\right) \| 0.85\mathrm{ZrO_2} + 0.15\mathrm{CaO} \| \mathrm{Co, CoO} \qquad (1)$$

In the original experiment, gas mixtures of CO and CO_2 were circulated over both the Fe-wüstite and Co-CoO electrodes and the measured emf was shown to be consistent with gas equilibration measurements. Subsequent measurements showed that the CO-CO_2 gas mixture was not always necessary and a metal-metal oxide mixture with a previously well-characterized Gibbs energy of formation could be used as a reference electrode to determine an unknown Gibbs energy of formation.[4] Similarly, a non-reactive gas electrode, such as Pt/O_2, could be used as a reference to determine the standard Gibbs energy change for the formation of oxides (*i.e.*, a Daniell type concentration cell).[5] This technique has been used to determine the Gibbs energy of formation for a variety of simple oxides (*e.g.*, Cu_2O, CoO, FeO, and Cr_2O_3).[6] Similarly, measurement of the activity of these oxides in mixed oxides has been used to measure the Gibbs energies of formation of ternary oxides (such as $CuCrO_4$),[7] and several orthoferrites ($YFeO_3$, $GdFeO_3$, and $SmFeO_3$).[8] This approach has also been used to construct the high temperature phase diagrams and establish the thermodynamic stability

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regimes for ternary[9] and quaternary[10] oxides of technological importance.

The Kiukkola and Wagner technique can also be used to measure the Gibbs energy of formation of non-oxide compounds, such as ZnTe and CdTe, which are used in semiconductor devices and optical applications. For example, the equilibrium activity of Zn in ZnTe can be established by equilibration with a fixed Te activity; and when this mixture is equilibrated with ZnO, the fixed Zn activity establishes an oxygen partial pressure, which can be measured by a galvanic cell with an oxide ion conducting electrolyte. This approach has been used with the following cell,[9]

$$\mathrm{Zn, ZnO} \,\|\, \mathrm{ZrO_2 - Y_2O_3} \,\|\, \mathrm{ZnTe{-}CdTe, M, ZnO} \qquad (2)$$

where M is Zn, Cd, or Te, which equilibrates with the ZnTe-CdTe pseudo binary system. Through judicious choice of M amongst the three metals, the composition of the ZnTe-CdTe within the two-phase field in the pseudo-binary system can be shifted from the Te-rich to the Te-poor side, which allows for characterization of the thermodynamic properties of the system. Figure 1 shows that the activity of Zn in the Te-rich region of the ZnTe-CdTe pseudo-binary system measured using the Kiukkola and Wagner technique is in excellent agreement with calculated activities.[11]

The original Kiukkola and Wagner technique has been modified to measure oxygen activity in molten metals, because dissolved oxygen in molten metals is of great metallurgical concern in controlling the microstructures and the final quality of products. The technique has been applied to pure metals as well as to alloys, including copper-tin, copper-nickel, and copper-silver,[12] for which, using Cu-Ni as an example, the galvanic cell is given by the following.

$$\mathrm{Pt, air} \,\|\, \mathrm{ZrO_2 - CaO} \,\|\, \mathrm{O(Cu - Ni)(liq), Mo} \qquad (3)$$

After correcting for the thermoelectric voltage (E_{th}) that is developed between the Pt and Mo leads, the voltage of the cell (E) can be directly correlated to the dissolved oxygen mole fraction (X_o) according to Eq. 4:

$$\mathrm{E} = \frac{\mathrm{RT}}{4\mathrm{F}} \ln\left(\frac{0.21K}{\mathrm{X_O}^2}\right) - \mathrm{E_{th}} \qquad (4)$$

where R is the gas constant, T is temperature, F is Faraday's constant, and K is the Henry's law constant for the oxygen dissolution reaction.

$$\mathrm{O_2\,(g)} \Leftrightarrow \mathrm{2O\,(alloy, liq)} \qquad (5)$$

Thus, calibration curves can be developed for each alloy system to determine Henry's law constant, after which Eq. 4 can be used conveniently to measure the dissolved oxygen activity. The solubility of oxygen as measured by the simple galvanic cell technique is in excellent agreement with that measured by other more time-consuming off-line analytical techniques.

A variation of the Kiukkola and Wagner technique employing a $MgAl_2O_4$ working electrode and systematically varying specific surface area has been used to measure the surface energy of $MgAl_2O_4$ [13] Although the technique has not yet been applied widely, it has the potential to measure surface energies using a simple experimental technique.

Transport measurements.—The Kiukkola and Wagner paper also led to improvement in the measurement of chemical diffusion in mixed ionic electronic conductors (MIECs), including alloys and ceramics, which are of practical interest for electrodes, catalysts, membrane reactors, and gas separation membranes. Ionic flux through these materials is determined by chemical diffusion in the presence of chemical gradients. However, accurate determination of chemical diffusion coefficients is not a trivial task. In general, small gradients are needed during these experiments to justify the assumption that the concentration dependence of the chemical diffusion coefficient can be neglected without significant error. In reality, however, large chemical gradients are necessary to impart measurable transport rates.

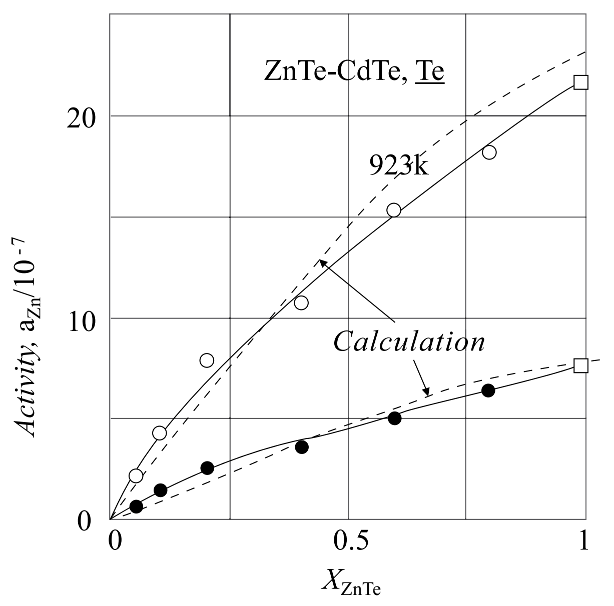

Fig. 1. *Activity of Zn in Te-rich ZnTe-CdTe pseudo-binary as a function of mole fraction of ZnTe.[11] Experimental data from the galvanic cells is shown along with computed activity-composition data from CALPHAD literature.*

This difficulty is largely overcome by invoking the central concept of the Kiukkola and Wagner paper, that electrochemical probes can accurately monitor activities at interfaces. This powerful tool allows one to change the activity of the electroactive species incrementally at solid electrolyte/MIEC interfaces. This concept, for example, has been used to measure lithium transport in prospective alloys and oxides for Li-battery electrodes,[14-16] and oxygen chemical diffusion in dense MIEC oxides for SOFC cathodes.[17]

The potentiostatic step technique was further refined to measure oxygen transport in MIECs[18] by coupling a thin slab of single crystal yttria stabilized zirconia (YSZ) to a sintered MIEC sample with appropriate seals against oxygen leakage as shown in Fig. 2. The electronically blocking YSZ/MIEC interface and the ionically blocking MIEC/Pt interface force one-dimensional oxide ion transport across the YSZ/MIEC interface when the equilibrium oxygen activity is perturbed by a small potentiostatic step that incrementally changes the initial concentration, C_o, to a new and fixed value, C_s, at the YSZ/MIEC interface. Cell current is monitored as the oxide ion activity in the MIEC sample relaxes to the new equilibrium, at which time the cell current decays to zero. Since electronic conduction in YSZ is negligible, the charge crossing the interface during relaxation is predominantly ionic in nature. The chemical diffusion coefficient can readily be extracted from the slopes of the short or long time approximations related to the solution of the one-dimensional Fick's 2nd law expression. Moreover, repetitious potentiostatic steps can establish an oxygen titration curve whose slope independently yields the thermodynamic enhancement factor, W, that relates the chemical diffusion coefficient, D, to the self-diffusion coefficient, D_O, for the oxide ions by $D = W \cdot D_O$, allowing independent determination of both diffusion coefficients. With further development, this approach was used to extract not only the chemical diffusion coefficient, but also the oxygen surface exchange coefficient on MIEC surfaces.[19]

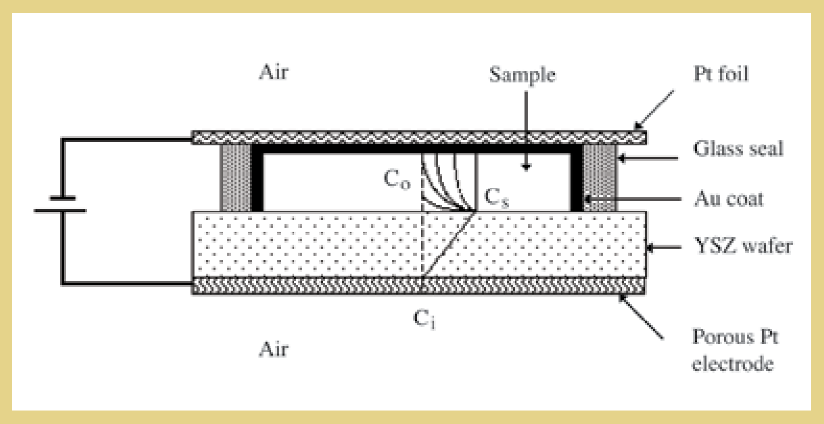

Fig. 2. *Schematic cross-section of solid state electrochemical cell for potentiostatic step measurement of oxygen chemical diffusion in MIEC oxides.*[18]

Catalysis.—Recognizing the potential impact of the Kiukkola and Wagner concept on catalysis, Wagner laid the groundwork for effective use of solid-state electrochemical tools in affecting the rates and selectivity of catalytic reactions.[20] In this seminal paper, Wagner pointed out that a catalytic surface exposed to a reacting mixture will eventually establish thermodynamic equilibrium between atoms on the surface and atoms in the bulk of the catalyst. Assuming transport between surface and bulk is sufficiently fast, one can monitor *in situ* the thermodynamic state of the surface species during a catalytic reaction by measuring a bulk property related to its activity. For example, under open circuit conditions, a YSZ electrolyte cell was used to monitor SO_2 oxidation on noble metal catalysts[21] and rate oscillations on Pt electrodes.[22]

Impact on Practical Applications

Enhanced catalysis.—The use of dc bias across a YSZ-based electrochemical reactor provides a means for "active" control, as opposed to "passive" monitoring, of surface oxygen activity for enhancing catalytic rates.[23] The central concept is applicable not only for thermodynamically favorable reactions, including NO decomposition[23] and Fischer-Tropsch synthesis,[24] but also for energetically uphill reactions, such as CO_2 methanation.[25] Reaction rate enhancements observed under this scheme are Faradaic in nature—that is, they scale with the amount of oxygen transported through the YSZ electrolyte. Since then, this electrochemical approach has been applied to a large number of catalytic reactions.[26]

Enhancements in the catalytic rates which exceed by several orders of magnitude that which could be expected from Faraday's law have been observed in what is referred to as the Non-Faradaic Electrochemical Modification of Catalytic (NEMCA).[27] In other words, a single oxide ion supplied to the catalyst surface can promote multiple reactions (up to 10^5). The NEMCA effect is related to a change in the work function of the catalytic electrode by the imposed bias, and is not limited to particular catalysts or solid electrolytes. Many reaction systems and cell materials exhibit this behavior.[28]

Chemical sensors.—After the work of Carl Wagner established the exclusively ionic conduction domain of zirconia over a wide range of oxygen partial pressure and its use in galvanic cells, practical industrial applications started to emerge quickly. In 1962, Westinghouse Corporation in the U.S. reported the use of zirconia-based solid state galvanic cells for an oxygen gauge and initial experiments on solid electrolyte fuel cells,[29] the fast response of which made zirconia based oxygen metering superior over other approaches. Subsequently, such devices became widely used for measuring and controlling combustion processes in boilers and industrial gases, which resulted in saving huge amounts of primary energy.[30] The probes also became commonly introduced in the ceramic and glass industries and are currently a standard to control the hardening of steel by controlling the carbon activity in CO/CO_2 gas mixtures by the equilibrium with oxygen.

The widest and most visible impact of Carl Wagner's paper has been on the Lambda (λ) Probe for controlling the emission of combustion engines by operating the catalyst under optimum air/fuel ratios (Fig. 3). This development was started at the end of the 1960s and early 1970s by General Motors in the U.S. and Brown Boveri and Bosch in Germany. Volvo first applied these sensors in California under the Clean Air Act in the early 1970s. The λ-probe became the first multibillion dollar business in the field of ionics and about 100,000 sensors are produced every day. Originally, the sharp voltage drop at the ideal air/fuel ratio (stoichiometric point) was used, but subsequently more sophisticated combined coulometric and potentiometric measurements were implemented to monitor the oxygen pressure in the lean burn regions. The response of this class of sensors is extraordinarily fast and unmatched by other techniques, and as such these sensors have been used for active feedback control of the combustion process. The sensors are now being considered for application in each individual cylinder.

Much less visible but equally important has been the impact of Carl Wagner's paper on the oxygen sensor development for industrial applications in post-war East Germany. The publication has prompted political support for work in this field as indicated by early patent applications on the technology.[31]

The high temperature stability and operation of solid electrolyte sensors has led to their use in molten metals. The most widely used is a zirconia based sensor for measuring the amount of dissolved oxygen in molten steel.[32] However, other electrolyte and electrode combinations allow for the measurement of other species, such as sulfur,[33] or alloying additions, such as sodium,[34] for improved control during the processing of the molten metals. The discovery of proton conducting oxides led to the development of electrochemical sensors for measuring the amount of hydrogen in molten aluminum, which is important for controlling the porosity of castings.[35]

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Fig. 3. *Lambda (λ) probe as originally developed by Bosch using doped zirconia as described by Kiukkola and Wagner.*[1]

A combination of the equilibrium and catalytic properties of solid electrolytes has been used in non-equilibrium chemical sensors that have the ability to measure the concentration of commercially important gas species such as carbon monoxide, hydrocarbons, nitrogen oxides, and ammonia. The electrode potential in such sensors is established by a steady state between oxidation and reduction reactions involving the oxygen-ion in the electrolyte. Although the reaction rates are primarily determined by the electrocatalytic properties of the electrode materials, the sensor output is the voltage generated across a solid electrolyte as in the equilibrium sensors described above.[36] While the potential is controlled primarily by the electrode material, it is also affected by the electrolyte material, so ceria, rather than zirconia, is used as the electrolyte in some sensors.[37] These sensors represent a combination of the galvanic cell and catalytic effects discussed above.

Fuel cells.—Carl Wagner's paper has also had an important impact on the development of high temperature fuel cells. Major research activities were initiated during the early 1960s especially at the Battelle Institutes in Frankfurt and Geneva, Westinghouse in Pittsburgh, and Siemens in Erlangen that continue through today.[38,39] Stabilized zirconia is the most commonly used electrolyte in SOFCs, the high operating temperature of which leads to excellent tolerance to the type and purity of fuel used. This fuel flexibility expands potential applications and impact by allowing SOFCs to be used with a wide variety of fuels including gasified coal and fuels derived from renewable biomass.[40]

Conclusions

Carl Wagner's contributions are remarkable in that they have both helped establish basic fundamental principles and led to important technological advances. The paper by Kiukkola and Wagner is just one example of such a contribution that has, over the past 50 years, led to an improved understanding of the thermodynamic, transport, and catalytic properties of materials as well as to practical applications in chemical sensing, energy conversion, and catalysis. ■

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Werner J. F. Weppner has long-standing experience in solid state electrochemistry since his doctorate at Dortmund University with Hans Rickert, a former close co-worker of Carl Wagner at Göttingen. After a postdoctoral period at Stanford University, he joined the Max-Planck-Institute for Solid State Research at Stuttgart and became a professor and Chairholder for Sensors and Solid State Ionics at the University of Kiel in 1993. His work covers a wide range of aspects of fast ion transport in solids from fundamental understanding, experimental techniques, materials characterization, development of new materials, and principles for practical applications in batteries, fuel cells, sensors, electrochromic devices, and photogalvanic solar cells. He is also involved in many professional activities including serving as Editor-in-Chief of the journal *Ionics*. He may be reached at ww@tf.uni-kiel.de.

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