Electrochemical Solid State Analysis: State of the Art

This Review is dedicated to Prof. Dr. Rolf Neeb on the occasion of his 65th birthday

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1 Introduction

Solid-state analysis relies largely on various spectroscopic and diffraction methods. There are no fundamental reasons for the lack of electrochemical methods for solid-state analysis – but there are practical reasons for this situation. Most importantly, until recently there were no handy methods available for the study of the electrochemistry of any solid sample, independent of its electrical conductivity, solubility, *etc.* Since electrochemistry always mirrors the thermodynamics and kinetics of interfacial reactions it follows that electrochemical measurements on solid compounds may provide valuable information concerning qualitative and quantitative composition, chemical equilibria, and kinetics of reactions of a solid compound. Of course, it is clear that we cannot get direct information concerning crystal structure, bond length, bond angles, *etc.*

Voltammetry, *i.e.* the recording of current *versus* electrode potential, has become the most important electrochemical measuring technique in the field of pure and applied electrochemistry. Jaroslav Heyrovský's direct current polarography, the first highlight of voltammetric analysis, was followed by a great variety of sophisticated techniques,[1] which have won an undisputed place in the arsenal of modern analytical chemistry. The historic roots of electrochemistry lay in studies of phenomena occurring at interfaces of solids with solutions. However, electro*analysis* was almost exclusively focused on solution studies with liquid mercury electrodes and the use of solid electrodes remained fairly limited.[2] The first studies of the electrochemistry of solids which were not metals, alloys, or semiconductors but insoluble metal oxides were performed as late as 1925.[3] To allow electro*analytical* studies of all solid substances, new experimental strategies had to be developed and new theoretical concepts for understanding this electrochemistry were necessary.

Potentiometric methods gave access to solubility products of sparingly soluble compounds in cases where electrodes of the second kind were amenable. Studies on galvanic cells with solid electrolytes provided access to thermodynamic data such as free energy of formation *etc.* of various solid compounds.[4] Obviously these methods are not suitable for the *analysis* of solid compounds, but they are part of fundamental electrochemistry.

This review is focused on the *analytical use* of voltammetry for the study of solid compounds. It does not intend to cover the research field of pure electrochemistry of solids. It seems that the latest developments in the field of voltammetry of solid substances have opened the way into a new world of electrochemistry. Nowadays it is reasonable to speak of *electrochemical solid-state analysis* as a field of research in its own right, and many interesting discoveries can be expected in the future from studies on the electrochemistry of solid substances.

2 Electrography. The Early Beginnings of Electrochemical Solid-state Analysis

In the late twenties of our century Glazunov and Fritz independently developed *electrography*, or as Fritz called it *Elektro-Tüpfelmethode* (electric spot test method).[5] The principle of electrography is that a sample of a metal, an alloy, or any other conductor, is anodically oxidized while being pressed against a sheet of paper which has been impregnated with a reagent. The sample is connected to the positive pole of a current supply and the negative pole is connected to a counter electrode. This counter electrode is a sheet of metal beneath the impregnated paper (see Figure 1). Through anodic dissolution of the sample,

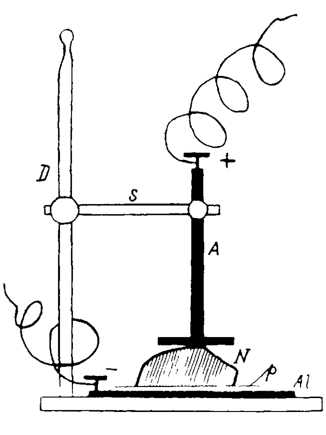

Figure 1 Equipment for electrography. A, anode; Al, cathode; N, mineral; p, paper with reagent.
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Birgit Meyer, née Lange, was born in Neustrelitz, Germany, and graduated with a Diplom in Chemistry from Humboldt University in 1990. Since 1991 she has been a Ph.D. student with Fritz Scholz. Her interest is focused on the electrochemistry of minerals with applications to mineral analysis.

metal ions are released from the sample and form coloured compounds with the reagent in the paper. In this way an image of the sample is produced which shows the distribution of, for example, nickel in a nickel ore, when dimethyl glyoxime is the reagent. Thus electrography was an early kind of spatial distribution analysis.

3 Compact Electrodes Made of a Solid Substance

This technique can be used only for solid materials which possess sufficient electrical conductivity and which can be manufactured into electrodes. Hence only metals, alloys, and semiconductors can be investigated by this technique. For analytical purposes the practical obstacles of this technique prevent a broader application. It is indeed laborious to make compact electrodes of solids, *i.e.* to shape them into a disc, to polish this disc, to mount the disc in a holder *etc.*, to make a voltammetric measurement on only one sample. Therefore *pressed cells* have been developed. These are electrochemical cells with a counter electrode, and possibly a reference electrode, in a cell without a bottom. Around the 'missing' bottom there is a rubber ring, so that the entire cell can be pressed against the metal surface which is to be studied (for a review of applications of pressed cells see reference 6). After filling the cell with electrolyte, measurements can commence.

A way of manufacturing compact electrodes from powders of conducting material is to press tablets, with or without a filling polymer.

In addition to the tedious procedures needed to make compact electrodes, there are other more fundamental reasons for not applying such electrodes to solid-state analysis. One of these reasons is that compact electrodes give rise to high currents. High currents can lead to iR-distorted voltammograms which hide information on thermodynamics or kinetics. In cases where there is more than one current signal, the resolution is poor and a multicomponent analysis can become impossible. High currents may also lead to unwanted chemical reactions on the surface of the electrode, *e.g.* the precipitation of compounds which cover the electrode surface and inhibit further electrochemical reactions. Published voltammograms obtained with compact electrodes often illustrate their unfavourable behaviour (Figure 2). For a review of applications of compact solid electrodes see references 7 and 8.

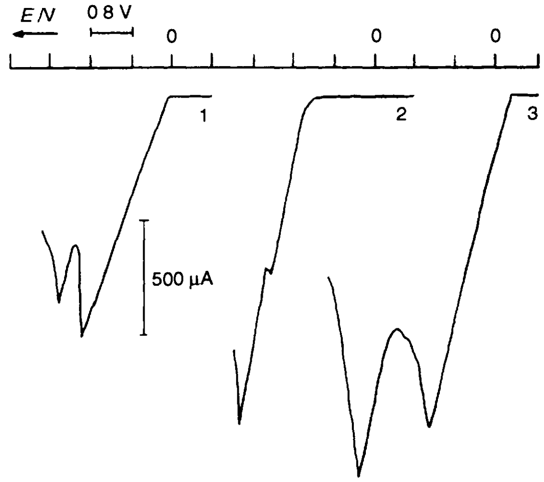

Figure 2 Anodic voltammograms of Cu–Sn alloys obtained with a pressed cell (1) 92.13% Cu, (2), 53.80% Cu, (3) 19.92% Cu. Note the potential scale!
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4 Carbon Paste Electrodes with Organic Binder and Addition of a Solid Substance

One way of partly overcoming the disadvantages of solid electrodes that have been mentioned is to use carbon paste electrodes. Here the solid compound is 'diluted' with graphite and formed to a paste with an organic binder. This has the advantage that there is a reduced amount of substance, and therefore the currents are smaller and surface coverage can be minimized. Kuwana and French[9] used this technique for voltammetric measurements on water-insoluble organic compounds, such as ferrocene or anthraquinone. The technique of modified paste electrodes has been extensively developed in the former Soviet Union by W. G. Barikov, O. A. Songina, N. F. Zakharchuk, and Kh. Z. Brainina. Several methods have been described for the quantitative analysis of powder mixtures, *e.g.* Ag_2O–AgO, cubic and hexagonal In_2O_3, iron–magnetite–wustite mixtures *etc.*[7] A highlight of the application of modified paste electrodes has been the determination of the composition of thin oxide films (2—100 nm) which form on GaAs by anodic oxidation or by thermal oxidation.[10] Figure 3 shows the published derivative d.c.-voltammograms. This figure illustrates how an identification of the following phases is possible: α-, β-, γ-, δ-, ϵ-Ga_2O_3, amorphous $Ga(OH)_3$, claudetite and arsenolite (both As_2O_3), α- and β-Sb_2O_3, As_2O_4, As_2O_5, Sb_2O_5, $GaAsO_4$, As and Sb (amorphous and crystalline), and Ga. When these results were published there were no other analytical spectroscopic techniques, including ESCA and Auger electron spectroscopy, which would have allowed the simultaneous identification of all these compounds. The thin film was mechanically removed with the help of diamond powder and the resulting mixture of film material and diamond powder was attached to the surface of a graphite paste electrode before commencing the voltammetric measurements. A recent review of the fundamentals and limitations of modified graphite paste electrodes discusses the influence of particle size on reproducibility of results and the entire procedure of paste preparation.[11] The influence of the organic binder on the electrochemistry of the solid compounds has not yet been fully elucidated, but in all probability the organic compound obscures, at least partly, the faradayic reactions of the solid compound (*cf.* the well-documented influence of adsorbed layers of surface-active compounds on the electrochemistry of dissolved species).

5 Carbon Paste Electrodes with Electrolytic Binder and Addition of a Solid Substance

In this technique the carbon paste electrode is formed using an electrolytic binder instead of an organic binder. So the exchange of electrons can in principle be achieved in the whole paste, not only at the paste–electrolyte interface. In practice the iR-drop within the paste will certainly restrict the electrochemical reaction to a layer of paste adjacent to the electrolyte solution. Such paste has to be housed in small cups with the upper surface exposed to the electrolyte solution, which has to be the same composition as the electrolytic paste binder. Bauer and Gaillochet[12] studied how the electrochemical behaviour of these electrodes depended on different parameters such as sweep rate, paste volume, and concentration of sample in the paste. They concluded that the solid itself is involved in the electrochemical processes. Lamache *et al.*[13] investigated the oxidation of Cu_2S in 1 M H_2SO_4 at very low scan rates and found that the oxidation proceeds in steps, forming copper sulfides of different stoichiometry (Figure 4). Some of these sulfides are minerals occurring in nature. Chouaib *et al.*[14] looked at the behaviour of different manganese oxides and they were able to distinguish different modifications through the different electrochemical reactions. Eguren *et al.*[15] have described a method for the determination of the β-SnO_2 contents in commercial tin dioxide. A review on carbon paste electrodes with an electrolytic binder has been published by Batanero *et al.*[16] Although paste electrodes do not suffer from the undesirable influence of organic compounds that

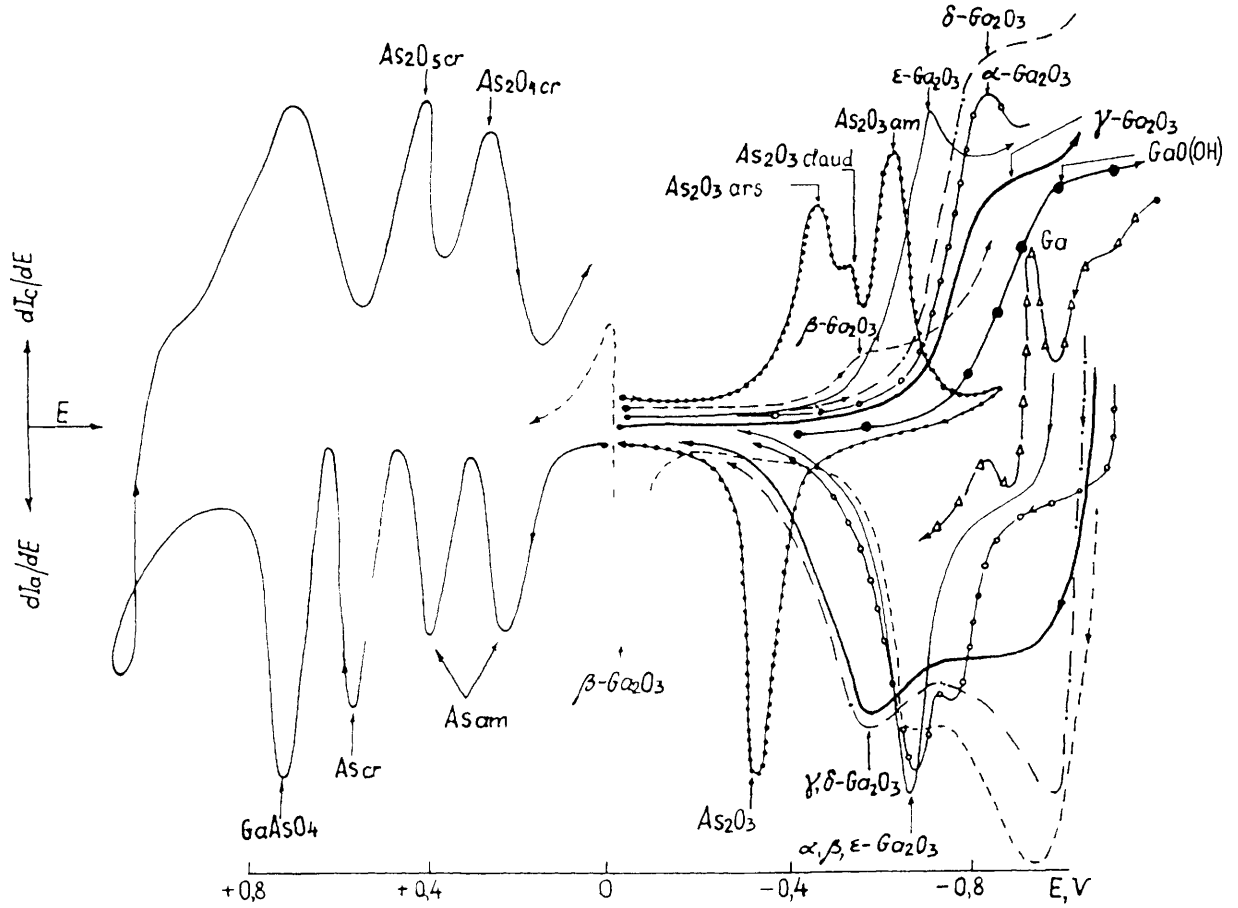

Figure 3 Spectrum of the standard substances for the Ga–As–O system obtained by cyclic voltammetry Measurements were performed in 3 M HCl for As, $GaAsO_4$, As_2O_5, and As_2O_4, in 1 M HCl for As_2O_3, and in 0 5 M HCl for Ga_2O_3, $Ga(OH)_3$, and Ga The reference electrode was a SCE
(Reproduced with permission from reference 10)

electrodes using organic binders experience, the electrolytic binder does need to be carefully chosen Very aggressive binders like mineral acids or bases, for example, may chemically dissolve the solid compound before the commencement of the electrochemistry, thus affording erratic results

6 Voltammetry of Suspended Solid Particles

Kolthoff and Stock[17] were the first to publish voltammograms of suspended silver bromide By chance Micka observed that suspended charcoal gives specific signals in polarography Later he and Kalvoda systematically investigated the polarography of various solid substances suspended in electrolyte solution [18 19] To keep the particles in suspension and to ensure that they can come into contact with the electrode surface, the suspensions have to be stirred Especially when a dropping mercury electrode is used, this stirring leads to very noisy voltammograms (see Figure 5) This problem can be circumvented by using a rotating disc electrode, the rotation of the electrode guarantees stable hydrodynamic conditions The results obtained by Micka indicated that the voltammetric response of suspensions is connected with the point of zero charge (p z c) because the suspensions gave peak-shaped current signals which were situated at or near the p z c Micka interpretated the peak-shaped curves as being due to an adsorption-like behaviour of the suspended particles at the electrode surface, the adsorption of the particles being greatest at the p z c Dausheva and Songina[20] were able to show that suspended particles of mercury iodide are strongly bound to the surface of a hanging mercury drop around the

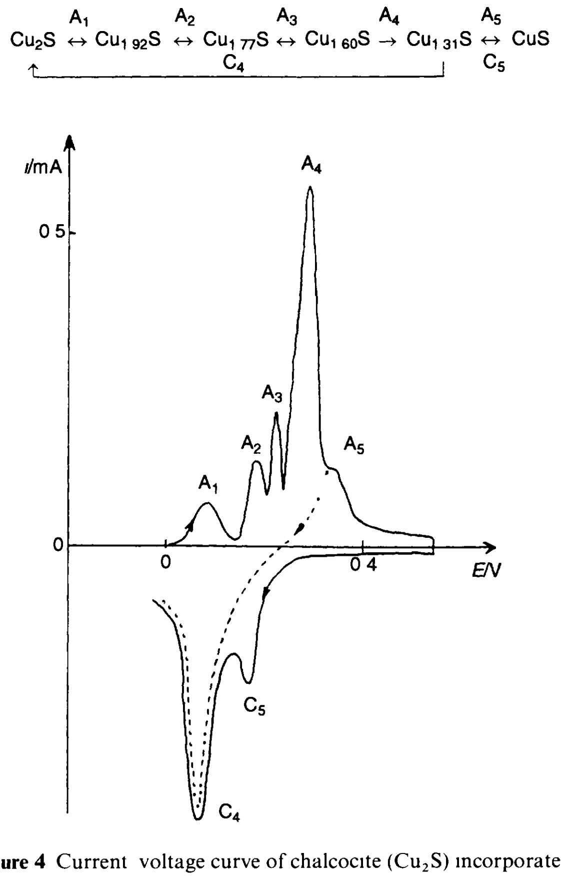

Figure 4 Current voltage curve of chalcocite (Cu_2S) incorporated in a carbon paste electrode with electrolytic binder Cu_2S (0 6 g), 1 M H_2SO_4 (40 mg) carbon (50 mg), scan rate 10 $^{-4}$ V/s
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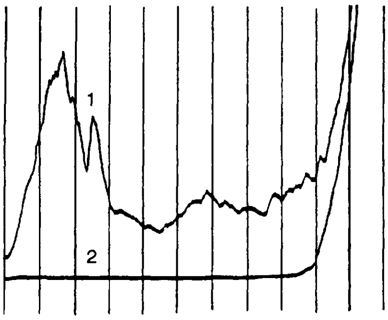

Figure 5 Reduction of manganese dioxide of the rutile type Twelve millilitres of 0 2 M H_2SO_4 + 6 mg MnO_2 (1), Electrically stirred suspension (2), Quit suspension Sensitivity 1/1000, beginning from 0 V, 200 mV/absc
(Reproduced with permission from reference 18)

p z c Applying the theory of Frumkin on the potential dependence of the stability of surface films they came to the following understanding At the p z c the electrolyte film between the electrode surface and the suspended particles has such instability that the particles can come into closest contact with the electrode, where they are deposited on the surface by electrocapillary forces They called this phenomenon *electrocapillary deposition* This deposition ensures that the particles come into such close contact that electrons can be transferred between the particles and the electrode At potentials far away from the p z c the stability of the electrolyte film is so high that even forced transport of the particles to the electrode surface by stirring is unable to bring the particles into closest contact with the electrode In this connection it should be remembered that some compounds become electro-inactive when they are in colloidal dispersion It is then probably impossible to disrupt the electrolyte film between the very small particles of the colloid and the electrode surface

7 Voltammetry of Solid Compounds Immobilized within a Polymeric Film on the Electrode Surface

Voltammetry of polymer films on electrodes has been extensively studied in the context of surface-modified electrodes, and the term *solid-state voltammetry* has been used for those systems in which redox-active sites are incorporated in the polymer film[21]

The idea of holding particles of a solid compound on the surface of a solid electrode by using a polymeric binder has been applied to the study of minerals[8] Franklin *et al*[22] have described the voltammetry of suspended solid compounds in cationic surfactant–styrene–aqueous sodium hydroxide emulsions using platinum electrodes Under these conditions a hydrophobic polymeric film is formed on the electrode surface which results in an enlarged potential window for measurements The solid particles are held on the electrode surface through the adsorption of surfactants embedding these particles From the literature it is not possible to answer the question of how the polymer film influences the electrochemistry of the solid particles The polymer film may have a negative effect on the voltammograms, but evidence for or against has not been given yet One thing however is certain – every measurement needs the preparation of a new electrode, which makes the technique rather inconvenient to use

8 Voltammetry of Solid Compounds Sandwiched between Two Solid Electrodes

Kulesza *et al*[23] have shown that solid compounds which possess ion conductivity and mixed valence sites give voltammetric signals when they are sandwiched between two solid electrodes Although no deliberately added electrolyte solution is present in these systems, the degree of hydration strongly influences the voltammetric response since a certain water content is essential for the ion mobility This kind of voltammetry has been described for metal hexacyanoferrates and single crystals of silicotungstic acid For hexacyanoferrates the voltammetric response is due to the following reactions

cathode $-Fe^{III}(CN)_{6(\text{site})} + e + K^+ \rightarrow -KFe^{II}(CN)_{6(\text{site})}$

anode $-KFe^{II}(CN)_{6(\text{site})} \rightarrow -Fe^{III}(CN)_{6(\text{site})} + e + K^+$

Thus it is electron hopping between the mixed valence sites and counter-ion flux which provides the current flow through the solid compound The electrochemistry is similar to that which is observed when a film of solid compounds, *e g* prussian blue, is deposited on a metal electrode and voltammograms are recorded in an electrolyte solution[24]

Since the described technique is limited to a small number of compounds, it cannot find a broader application for analysis, but the results of these studies are very valuable for understanding the electrochemistry of solid compounds and will be of benefit for other techniques as well

9 Abrasive Stripping Voltammetry

Abrasive stripping voltammetry (AbrSV) is a new approach for the direct study of solid samples which has recently been introduced by Scholz *et al*[25] It makes use of the fact that (from Faraday's law) extremely small amounts of a sample are sufficient to give easily measurable currents The use of paraffin-impregnated graphite electrodes to fix such small amounts of solid particles on an electrode surface has proved to be very successful, although in principle any solid electrode is suitable The transfer of the solid compound can be achieved simply by abrasion, after which small solid particles stick to the electrode surface For the fabrication of paraffin-impregnated graphite electrodes (PIGE), soft graphite rods are put into molten paraffin under vacuum until air bubbles cease to evolve from the rods After re-establishing atmospheric pressure the rods are removed before the paraffin solidifies For transfer of the solid sample to the electrode surface, the solid compound is powdered and placed on a glazed porcelain tile and spread out with an agate mortar to form a spot of finely distributed material Then the lower circular end of the PIGE is gently rubbed over that spot of sample Trace amounts, down to about 10^{-6} to 10^{-11} mol of sample, are mechanically immobilized on the electrode surface Effective abrasion is often also possible by rubbing the electrode on a smooth surface of a solid, even when this is harder than the electrode surface In the case of an extremely hard material, corundum powder may be added to support the abrasion

After the transfer of the solid sample to the electrode surface the electrode is dipped into a conventional electrochemical cell with auxiliary and reference electrodes so that only the circular surface of the electrode is in contact with the electrolyte solution (see Figure 6) In this way it is possible to achieve good

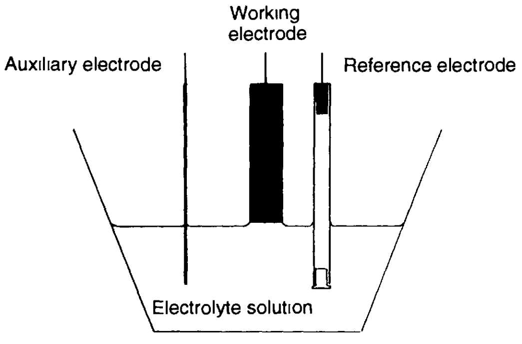

Figure 6 Electrochemical cell for abrasive stripping voltammetry

reproducibility of the background current and an almost constant electrode area. After the measurement, the electrode is cleaned by rubbing the surface on filter paper. The effectiveness of the cleaning procedure can be checked by recording a blank voltammogram.

All the usual electrochemical techniques can be carried out by AbrSV. Thus, for example, the oxidation or reduction of solid compounds can be studied and used for analytical purposes. In addition it is possible to record so-called *inverse* voltammograms. This technique involves reducing the cations of a solid compound to metals which become deposited on the electrode surface.[26] and in the following anodic voltammogram anodically dissolving the metals in the electrolyte solution. The oxidation peaks obtained allow qualitative identification of the elements and quantification of composition of the solid (*cf.* Figure 7). By coprecipitation of mercury from the electrolyte solution during the reduction of a solid metal compound, the metals formed dissolve in the *in situ* plated mercury droplets on the electrode surface and the resolution of the following anodic voltammograms is remarkably improved. This technique results in relative standard deviations in quantitative analysis as low as 0.5%.[27] Such voltammograms with *in situ* plated mercury are identical to the anodic stripping voltammograms which are well documented for mercury electrodes.

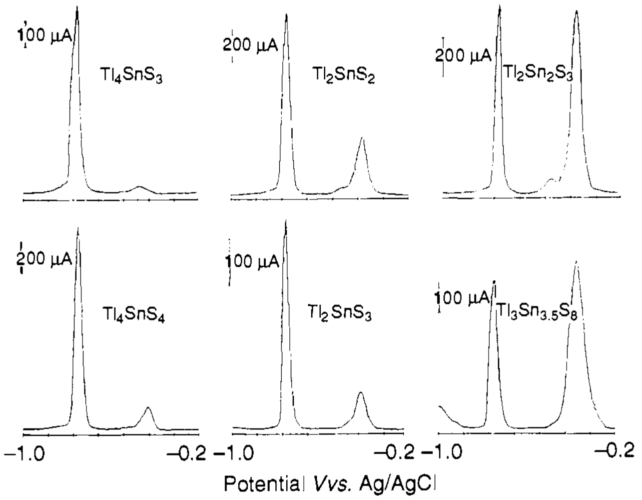

Figure 7 Inverse abrasive stripping voltammograms of different Tl – Sn sulfo-salts in 1 M HCl. Scan rate 0.01 V/s, deposition potential − 1.0 V, deposition time 60 s, differential pulse modus.

AbrSV can be applied to all solid compounds which contain at least one electrochemically active element. Experiments were initially conducted on pure metals and simple alloys. Anodic dissolution peaks occur at potentials which are characteristic for the metals in specific electrolytes and allow their identification. In the case of alloys, one can obtain qualitative information on the elemental constituents, provided that there are no strong interactions between the constituents in the solid phase. When intermetallic phases are present they can be identified by their specific signals. Quantitative determination of the alloy constituents is possible because the peak height ratios of the alloy constituents depend on the composition.[25] For this a calibration plot is necessary. AbrSV also provides information on the electrochemical corrosion behaviour of alloys. Detailed studies have been undertaken on dental amalgams.[28] The results showed unambiguously that the corrosion of dental amalgams containing the often blamed γ_2-phase ($Sn_{7-8}Hg$) is only worse than that of γ_2-phase-free amalgams when the electrolyte does not contain strongly complexing ions. In solutions with a high concentration of citric acid (*e.g.* beverages) γ_2-phase-free and γ_2-phase-containing amalgams have the same stability.

A fascinating field of application is the voltammetric identification and analysis of minerals.[26] With AbrSV, qualitative information on the metallic constituents is accessible from an inverse voltammogram, provided that no intermetallic phases are formed during the reduction. Every voltammogram is a voltammetric fingerprint for a particular mineral in a specific electrolyte; unambiguous identification of minerals can thus be achieved. Where there are different modifications of a mineral, it is impossible to distinguish between them by conventional electrochemistry after digestion, because the same solution results. In AbrSV however the solid substance is not destroyed before analysis and therefore the influence of the structure of the solid on the electrochemistry is not lost. Thus different modifications give different voltammograms. This is not true for *inverse* AbrSV, which therefore cannot be used to distinguish between different modifications.

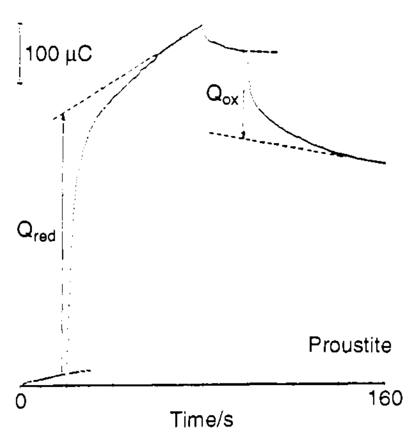

Figure 8 Abrasive stripping coulogram of mechanically transferred proustite in 1 M KCl. Potentials: − 0.6 V (20 s), − 1.1 V (60 s) (reduction of proustite), − 0.6 V (20 s), 0.2 V (60 s) (oxidation of silver).

In some cases it is possible and useful to perform coulometric measurements. Figure 8 depicts a coulogram of mechanically transferred proustite from which the ratio of charges for reduction ($Ag_3AsS_3 + 9e^- + 3H^- \rightarrow 3Ag + AsH_3 + 3S^{2-}$) to the charge for subsequent oxidation of the Ag ($3Ag \rightarrow 3Ag^+ + 3e^-$) formed can be easily derived.[29] In some special cases, if the electrochemistry is reversible, it is possible to calculate thermodynamic data for minerals.[30] AbrSV is a valuable technique for the study of insoluble substances and provides hitherto inaccessible information on the electrochemistry and chemistry of such compounds. As an example, it was possible to compare the electrochemistry of mercury and lead dithiocarbamates in dichloromethane solution with the electrochemistry of the solid compounds at the aqueous electrolyte electrode interface. It turned out that during cyclic reduction of the dithiocarbamates and oxidation of the deposited metals to the dithiocarbamates, the formal potentials of these redox systems were determined by the conditional brutto stability constants of the complexes. These thermodynamic data could be easily determined and comparison with some known values of complexes showed excellent agreement.[31,32] Bond *et al.*[33] used the technique of abrasive stripping voltammetry in a detailed study of the electrochemistry of solid microcrystalline *cis*- and *trans*-$Cr(CO)_2(dpe)_2$ and *trans*-$[Cr(CO)_2(dpe)_2]^+$ complexes (dpe = $Ph_2PCH_2CH_2PPh_2$). Those compounds are entirely insoluble and they are electrical insulators. Nevertheless they give well-defined voltammograms when mechanically attached to a pyrolytic graphite electrode (see Figure 9). With the help of *X*-ray electron probe analysis it was shown that the oxidation of these complexes is accompanied by the incorporation of perchlorate ions into the lattice of the solid compounds. In a similar way to the behaviour of the sandwiched hexacyanoferrates, electron hopping between the metal centres occurs and electroneutrality is provided by a flux of counter ions. The chromium complexes differ from the hexacyanoferrates in that the former are not ion conductors and do not contain water. Dueber *et al.*[34] have used AbrSV to study

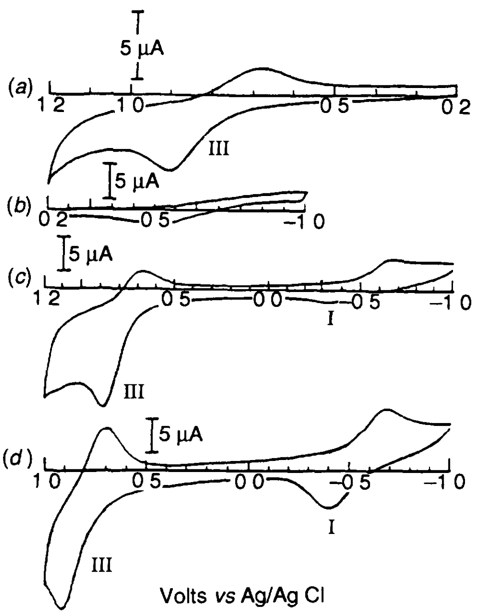

Figure 9 Cyclic voltammograms obtained in aqueous (0 1 M $NaClO_4$) media at 20 °C for solid *trans*-$[Cr(CO)_2(dpe)_2]^+$ mechanically attached to a polished basal plane pyrolytic graphite electrode (scan rate 50 mV/s) (a) Initial and final potential = 0 2 V, switching potential = 1 2 V, (b) initial and final potential = 0 2 V, switching potential = 1 0 V, (c) first cycle, initial and final potential = − 1 0 V, switching potential = 1 2 V vs Ag/AgCl, (d) as for (c) but six cycles (Reproduced with permission from reference 33)

the intercalation of magnesium ions into uranium oxides The investigation of electrochemically-induced intercalation of ions into a host lattice is of utmost importance for the design of rechargeable batteries

AbrSV has also proved to be applicable to the quantitative analysis of powder mixtures [35]

Another group of compounds which has been studied by AbrSV is that of the high-temperature superconductors It was found that in the case of YBaCu high-T_c superconductors, superconductivity was observed only when Cu^{3+}/Cu^{2+} and Cu^{2+}/Cu^{+} couples were present [36]

The theory of AbrSV has been addressed by Lovric *et al* [37 38] for the case of square-wave voltammetry of immobilized reactants, and by Jaworski *et al* [39] for linear-sweep voltammetry of reversible reduction of metal salts For a review on abrasive stripping voltammetry see reference 35

10 Mechanistic Considerations Concerning the Electrochemistry of Solid Compounds

Faradayic reactions of solid compounds at the interface with an electrolyte solution, *i e* reactions involving an electron transfer between an inert electron conductor and a solid compound, may proceed along different pathways They are always accompanied by an ion transfer between the solid phase of the reacting compound and the adjacent solution phase to preserve charge equilibrium in each phase The reaction pathway of a solid compound depends first on its electron conductivity In the case of a sufficient electron conductivity, faradayic reactions can proceed directly on the surface of the solid compound Examples are the anodic dissolution of a metal like copper, the reduction of lead ions in solid lead sulfide PbS, and also the oxidation of sulfide ions in the latter compound When copper is oxidized the copper ions are transferred into the electrolyte phase and the solid copper phase dissolves When the lead ions of PbS are reduced to metallic lead, this metal forms a new solid phase and the sulfide ions are transferred into the electrolyte phase The oxidation of sulfide ions of PbS leads to the formation of a new solid elemental sulfur and the transfer of lead ions into the solution phase

In the case of solid compounds with an insufficient electron conductivity, the faradayic reactions are more difficult to understand The transfer of electrons can only proceed at the interface of the inert electrode and the solid compound when there is also the possibility for an exchange of ions between the solid compound and the solution phase This is easily possible at those places where the three phases – inert electrode, solid compound, and electrolyte solution – are in contact with each other A similar mechanism is known for electrochemical reactions in emulsions [40] Some solid compounds possess the ability to conduct electrons by intra- or intermolecular redox reactions within the solid compound This electron hopping has to be accompanied by a flux of ions to preserve the charge neutrality Compounds which follow such a mechanism include the Prussian Blue analogue compounds and the organic chromium compounds discussed above

In case of solid compounds which are sparingly soluble (or not fully insoluble) it can be observed that dissolved species undergo electrochemical reactions at the surrounding electrode surface When the product of this electrode reaction is again insoluble, as is the case when dissolved lead dithiocarbamate is reduced to lead metal, a restructuring of the electrode surface takes place in the course of cyclic polarization

Besides the direct electrochemical reactions of solid compounds, a mediated reduction or oxidation of solid compounds on the electrode surface is possible Hydrogen, in particular, has been suggested to be the mediator for the reduction of metal salts

11 Conclusions

Electrochemistry now possesses many experimental tools for the study of phenomena at the interface between solid compounds and electrolyte solutions This experimental basis makes possible an almost infinite number of new experimental investigations and challenges our theoretical understanding of electrochemical phenomena It is to be expected that many branches of science will benefit from these developments In analytical chemistry, both organic and inorganic, direct solid-state analysis using electrochemical techniques will be attractive for many practical applications Battery and fuel cell development can benefit from solid-state electrochemical measurements because they enable the clear elucidation of electrode reactions Materials science and corrosion science get new tools for the characterization of materials and for the study of their electrochemical corrosion Mineralogy gets microanalytical techniques for the identification and analysis of mineral phases, even for the most tiny amounts Moreover, mineralogy can use these electrochemical techniques to get access to the chemical and electrochemical reactions of minerals which are otherwise difficult to study

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12 References

1 'Analytical Voltammetry', ed M R Smyth and J G Vos Vol 27 of 'Wilson and Wilson's Comprehensive Analytical Chemistry , ed G Svehla, Elsevier, Amsterdam, London, New York Tokyo 1992
2 A M Bond and F Scholz, *Z Chem* 1990, **30**, 117
3 K Fischbeck *Z Anorg Allg Chem* 1925 **148** 97
4 H Rickert, 'Electrochemistry of Solids An Introduction Springer Verlag, Berlin, 1982
5 R Jirkovsky, *Mikrochemie*, 1934, **15**, (N F **9**) 331
6 V V Slepushkin, *Zh Anal Khim* 1987 **42** 606

7 Kh Z Brainina, E Ya Neyman, and V V Slepushkin, 'Inversionnye elektro analiticheskie metody', Khimiya, Moskva, 1988

8 V A Chanturiya and V E Vigdergauz, 'Elektrokhimiya sulfidov, teoriya i praktika flotatsii', Nauka, Moskva, 1993

9 T Kuwana and W G French, *Anal Chem* , 1964, **36**, 241

10 V I Belyi, T P Smirnova, and N F Zakharchuk, *Appl Surf Sci* , 1989, **39**, 161

11 W Gruner, J Kunath, L N Kalnishevskaja, J V Posokin, and Kh Z Brainina, *Electroanalysis*, 1993, **5**, 243

12 D Bauer and M Ph Gaillochet, *Electrochim Acta*, 1974, **19**, 597

13 M Lamache and D Bauer, *Anal Chem* , 1979, **51**, 1320

14 F Chouaib, O Cauquil, and M Lamache, *Electrochim Acta*, 1981, **26**, 325

15 M Eguren, M L Tascon, M D Vazques, and P Sanchez Batanero, *Electrochim Acta*, 1988, **33**, 1009

16 P Sanchez Batanero, M L Tascon Garcia, and M D Vazques Barbado, *Quimica Analitica*, 1989, **8**, 393

17 I M Kolthoff and J T Stock, *Analyst*, 1955, **80**, 860

18 K Micka, in 'Advances in Polarography', Proceedings of the 2nd Int Congress on Polarography, Cambridge 1959, ed I S Longmuir, Pergamon Press, New York, Oxford, London, Paris, 1960, Vol 3 (1959), pp 1182—1190

19 R Kalvoda, in ref 18, pp 1172—1181

20 M R Dausheva and O A Songina, *Usp Khim* , 1973, **42**, 323

21 T T Wooster, M L Longmire, H Zhang, M Watanabe, and R W Murray, *Anal Chem* , 1992, **64**, 1132, and references cited therein

22 T C Franklin, J Darlington, R Nnodimele, and R C Duty, in 'Electrochemistry in Colloids and Dispersions', ed R A Mackay, J Texter, VCH Publishers, Inc , New York, 1992, pp 319—329

23 P Kulesza and Z Galus, *J Electroanal Chem* , 1992, **269**, 261

24 D N Upadhyay and D M Kolb, *J Electroanal Chem* , 1993, **358**, 317

25 F Scholz, L Nitschke, and G Henrion, *Naturwissenschaften*, 1989, **76**, 71

26 F Scholz, L Nitschke, G Henrion, and F Damaschun, *Fresenius Z Anal Chem* , 1989, **335**, 189

27 F Scholz and B Lange, *Fresenius J Anal Chem* , 1990, **338**, 293

28 F Scholz, F Rabi, and W -D Muller, *Electroanalysis*, 1992, **4**, 339

29 S Zhang, B Meyer, G Moh, and F Scholz, *Electroanalysis*, in press

30 B Lange, F Scholz, H -J Bautsch, F Damaschun, and G Wappler, *Phys Chem Minerals*, 1993, **19**, 486

31 A M Bond and F Scholz, *J Phys Chem* , 1991, **95**, 7460

32 A M Bond and F Scholz, *Langmuir*, 1991, **7**, 3197

33 A M Bond, R Colton, F Daniels, D R Fernando, F Marken, Y Nagaosa, R F M Van Steveninck, and J N Walter, *J Am Chem Soc* , 1993, **115**, 9556

34 R E Dueber, A M Bond, and P G Dickens, *J Electrochem Soc* , 1992, **139**, 2363

35 F Scholz and B Lange, *Trends Anal Chem* , 1992, **11**, 359

36 S Scheurell, F Scholz, T Olesch, and E Kemnitz, *Supercond Sci Technol* , 1992, **5**, 303

37 M Lovric, S Komorsky-Lovric, and A M Bond, *J Electroanal Chem* , 1991, **319**, 1

38 S Komorsky-Lovric, M Lovric, and A M Bond, *Anal Chim Acta*, 1992, **258**, 299

39 A Jaworski, Z Stojek, and F Scholz, *J Electroanal Chem* , 1993, **354**, 1

40 H Fees and H Wendt, *Ber Bunsenges Phys Chem* , 1981, **85**, 914