

ELECTROCHEMISTRY OF IMMOBILIZED MICROPARTICLES AND MICRODROPLET: ACCESS TO FUNDAMENTAL DATA OF SOLID MATERIALS AND IONS

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The idea to study the electrochemistry of immobilized microparticles has been published by this author for the first time in 1989. In the last 32 years, this approach has been shown to be very successful not only for analytical characterization of solid materials, but also applicable to extract thermodynamic and kinetic data, and even to determine the age of metal specimen. In 2000, it has been shown that the electrochemistry of immobilized microdroplets gives an elegant access to determine the Gibbs free energies of ion transfer between immiscible solvents. These measurements are performed with a standard 3-electrode potentiostat and can be used also for solvents, which cannot be used in experiments with the classical 4-electrode technique.

The electrochemistry of microparticles and microdroplets share several common features with respect to the electrode mechanisms: in both cases three-phase electrodes are realized and ion and electron transfer proceed simultaneously.

This talk reviews the activities of the speaker and his cooperation partners during the last 3 decades paying special attention to those results, which are of general interest.

Key words: Electrochemistry of solids, three-phase electrodes, ion transfer between immiscible solvents.

Electrochemistry of immobilized microparticles

The electrochemical analysis and characterization of solid materials has always been a great challenge; however, it remained confined to electron conductors, mainly metals; it was and still is the domain of corrosion science. The last decades have also seen tremendous advances in the insertion electrochemistry of solid materials for batteries, almost exclusively studied with compact macroscopic solid electrodes.

Among the many attempts to expand the applicability of electrochemical measurements to solids, the early work of the Russian scientist A. I. Glazunov [1] is noteworthy. He called his technique *electrography*. A more detailed review of the history of solid state electroanalysis is available elsewhere [2]. Then, in 1989, Scholz, Nitschke and Henrion [3] have shown that metal particles can be transferred from a piece of metal to the surface of a graphite electrode by abrasion, i.e., by rubbing the graphite electrode on the surface of the metal, and soon after, the same authors have shown together with Damaschun that also mineral particles can be mechanically immobilized on an electrode for electrochemical studies [4].

The purely analytical applications, i.e., the *quantitative analysis* of alloys, minerals and synthetic solid materials will not be discussed here, as it is presented in detail in [2]. Instead, attention is drawn on the possibility to determine the free energies of phase transition in case of some minerals, when the two phases can undergo reversible electrochemical reactions to the same dissolved species [5, 6]. Studies of immobilized microparticles also allowed to understand the dependencies of formal po-

tentials on structure parameters as ionic radii and ion potentials, in case of polycyanometalates [7, 8]. Another noteworthy topic is the electrochemical study of solid solutions [9–12]. Whereas X-ray diffraction of solid solutions requires a certain degree of crystallinity, the electrochemical approach also works in case of X-ray amorphous substances (see [10]).

A number of theoretical papers have been published in which the mechanism of electrode reactions of immobilized microparticles is treated [13–17].

The electrochemical behavior of microparticles has also been studied by *in-situ* combination with X-ray diffraction [18], calorimetry [19, 20], diffuse reflection spectroscopy [21], and AFM [22–27]. These combinations allowed distinguishing the different electrode mechanisms. The studies of the electrochemistry of microparticles led to the development of an approach for separating the Gibbs free energies of ion and electron transfer in case of reversible insertion electrochemical systems [28, 29].

Finally, it is noteworthy to mention that the electrochemistry of microparticles gives access to the age of metal objects, be they of gold, copper, bronze, or silver [30]. These electrochemical age determinations are of very special value because so far almost no *direct* methods of age determinations of metals and alloys were known.

Electrochemistry of immobilized micro-droplets

When a droplet of an immiscible solvent is immobilized on a suitable electrode, and when that droplet contains a redox active com-

pounds, but no salt, an electron transfer between the redox probe and the electrode initiates an ion transfer between the bulk electrolyte solution and the droplet solvent. Similar to the insertion electrochemistry of microparticles, the entire electrode is a three-phase electrode. When the formal potential of the redox probe in the droplet solvent is known, simple voltammetric measurements with the immobilized microdroplets allow determining the Gibbs free energies of transfer of the ions, which are transferred between the solvents [2, 31–43]. This approach allowed to determine the Gibbs energies of ion transfer, i.e., the partition constants, of ions between water and n-octanol [32, 39], which is not possible when using the classical 4-electrode systems. It was possible to quantify the chiral recognition energies for ions using the solvent system water / chiral organic solvent [33, 42]. Amino acid anions, cations and also peptide ions have been studied in order to quantify the lipophilicity of these ions and their constituents [36, 38]. The new technique of using immobilized droplet electrodes considerably expanded the range of ions and of solvents for which Gibbs free energies of ion transfer are accessible.



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ЕЛЕКТРОХІМІЯ ІММОБІЛІЗОВАНИХ МІКРОЧАСТИНОК І МІКРОКРАПЕЛЬ: ПІДХІД ДО ФУНДАМЕНТАЛЬНИХ ДАНИХ ТВЕРДИХ МАТЕРІАЛІВ ТА ІОНІВ

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Ідею вивчення електрохімії іммобілізованих мікрочастинок було вперше оприлюднено автором роботи в 1989 році. Отже, за останні 32 роки цей підхід показав себе дуже успішним не тільки для аналітичних характеристик твердих матеріалів, а й для застосування при отриманні термодинамічних і кінетичних даних і навіть визначення віку металевих зразків. У 2000 році було показано, що електрохімія іммобілізованих мікрокрапель дає надійний доступ для визначення вільних енергій Гіббса – переносу іонів між незмішуваними розчинниками. Ці виміри проводять із використанням стандартного триелектродного потенціостата і їх можна застосувати також для розчинників, які не можливо використовувати в експериментах із класичною чотириелектродною технікою. Електрохімія мікрочастинок і мікрокрапель має кілька спільних рис відносно електродних

механізмів: в обох випадках реалізуються трифазні електроди і перенесення іонів та електронів відбувається водночас. У повідомленні представлено результати діяльності спікера і його партнерів зі співпраці за останні 3 десятиліття, особливу увагу приділено результатам, які становлять спільний інтерес.

Ключові слова: електрохімія твердих тіл, трифазні електроди, іонний перенос між незмішуваними розчинниками.

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