REVIEW

The electrochemistry of particles, droplets, and vesicles – the present situation and future tasks

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Abstract Presently, a plethora of techniques is available to study the electrochemical properties of solid inorganic and organic micro- and nano-particles *immobilized* on electrode surfaces, provided that they possess a faradaic electroactivity. Similarily, immobilized droplets of liquids and solutions, which are immiscible with the electrolyte solution, give access to the three-phase electrochemistry of redox centers in the droplets, allowing determinations of free energies of ion transfer between the immiscible liquid phases. Possible and necessary future activities in the field of immobilized particles and droplets will be discussed here. The electrochemistry of *suspended* micro- and nano-particles possessing faradaic electroactivity is much more complex and needs special

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attention in future research. Finally, the electrochemistry of liposomes and biological vesicles, which do not possess faradaic activity, but the ability to produce capacitive signals upon attachment to electrodes, will be discussed focusing on possible future developments.

The electrochemistry of immobilized solid micro- and nano-particles, and droplets

Present situation

For a very long time, electrochemists were either interested in the electrochemical properties of compact solid materials (e.g., battery materials, metal deposition, metal dissolution, etc.) or in the electrochemical properties of dissolved compounds. Studies of the electrochemical properties of particles started much later, possibly because people did not see the need, and only for reasons of scientific curiosity, some tried colloidal suspensions, etc. To safe precious journal space, I refer to some reviews in which the early time of "particle electrochemistry" is discussed [1–3]. With the introduction of the simple technique of immobilizing solid particles and liquid droplets on electrodes, the applicability of electrochemistry could be extended to materials of very low electronic conductivity (even insulators) because the reaction can proceed at extended three-phase junctions where a potential control "in" the solid particle or liquid droplet is possible [4–6]. This enabled studies of compounds, which were before inaccessible for

electrochemistry, at least as solid compounds. A few examples may be listed here: indigo [7], TCNQ micro-crystals [8–11], Maya blue [12, 13], manganese(IV) centers in archeological glasses [14], fine-grained iron oxides in environmental samples [15], iron oxide pigments [16], metal organic compounds [17–21], zeolites [22, 23], doped zirconium oxide [24], solid diphenylamine crystals [25], solid carbazole crystals [26], ruthenium (III) trichlorid solid crystals [27], and many redox liquids, e.g., [28, 29]. The clear message of these and many other studies is: If you have a solid compound (material), which is too resistive to make a conventional electrode out of it, you can be successful when using it as a fine powder. In case of liquids, you need to immobilize fine droplets on the electrode surface. The latter approach led to a new way of determining free energies of ion transfer between immiscible liquids [3, 30–32]. Very recently, Domenech et al. [33] have reported an ingenious method for determining ion transfer energies between *miscible* solvents by making use of a solid state insertion electrochemical reaction. The technique of mechanical attachment proved to be very efficient for a fast evaluation of the charge/discharge abilities of battery materials [34, 35]. In addition to the ability to study otherwise not accessible materials, I see some other advantages of the technique of immobilization of particles on electrodes:

1. The mechanical immobilization exposes the particles to the electrolyte solution without any—possibly harmful—effect of binders, as it may happen with paste and composite electrodes.
2. It is possible to study large series of chemically synthesized compounds in order to discover structure-reactivity relationships. Early examples are studies of hexacyanometalates [36, 37]. They revealed that the insertion electrochemistry of the solid hexacyanoferrates is directly correlated with the electrochemistry of dissolved hexacyanoferrates. Later examples are structure-reactivity relationships for complex hexacyanometalates [38].
3. The technique of immobilized particles allows systematic studies of series of solid solutions [28, 39, 40]. The ability of electrochemistry to clearly distinguish between solid solutions (one phase) and phase mixtures, even when the solids are x-ray amorphous [41], is a special highlight.
4. The technique allows studies with material amounts down to 10^{-11} mol [42]. This is especially valuable for the electrochemical identification of the tiniest amounts of minerals [43].
5. The technique can be easily combined with in situ microscopic, spectroscopic, and calorimetric techniques [44–50].

Future perspectives

It is always easier to describe the past than to make some forecast of future work. However, I like to make some suggestions in what direction electrochemical studies of solid particles should be expanded:

1. So far, the electrochemistry of immobilized particles and droplets [3] did essentially still showed the bulk behavior of the particles. It will be thrilling to extend such studies to so small particles that the electrochemistry will be governed by the thermodynamics of the surface.
2. The dynamics of electrochemical solid-to-solid inter-conversions involving moving interfaces has been addressed in a few papers [4, 51–54]; however, both theoretical calculations on a quantum-mechanical basis and further experimental studies [55] on a single particle basis still need to be done.
3. The problem of immiscibility gaps in electrochemical solid-to-solid interconversions has been theoretically analyzed [56], but only one experimental study, in which compounds exhibit the foreseen behavior, has been published [57]. Clearly, it is desirable to study more systems with miscibility gaps.
4. In case of immobilized particles, it is necessary to search for more structure-reactivity relationships, by carefully analyzing the electrochemical properties of well-defined series of synthesized compounds. It will be very interesting how structure (bond) variations affect the thermodynamic properties (e.g., formal potentials) and the rate constants of electrochemical reactions of the solid compounds. This work should be supplemented by quantum chemical calculations.
5. Extending the work on solid solutions will enable to determine thermodynamic excess data in case of non-ideal mixing (which is the normal case).
6. The study of solid solutions of x-ray amorphous and crystalline compounds may give access to the free energy changes due to crystallization.
7. The technique should be used for screening electrode materials for electrocatalytic or battery applications. Even a high-throughput-screening may be realized.
8. The technique can be used to study chemical reactions of particles with dissolved species using electrochemical, spectroscopic, and microscopic techniques in combination. So far, only the chemical oxidation of immobilized lead particles has been reported [58].
9. Although some single particle studies have been published, e.g., [59–61] this topic for sure deserves more attention, especially to understand the reactivities of different crystal faces.

10. The nucleation-growth kinetics of electrochemical solid-to-solid conversions [38, 62, 63] should be studied for many more systems, in order to understand the underlying principles.
11. The use of immobilized particles, exhibiting insertion electrochemistry for determining free energies of ion transfer between immiscible solvents [33], deserves a wide exploitation.
12. The electrochemistry of particles, suspended in solutions, is still a largely undiscovered research field. The interaction of suspended particles with an electrode surface is affected by their own electrochemical double layer, by the electrode double layer, and by their ability to undergo faradaic reactions, or to attach to the electrode surface without faradaic reaction causing only capacitive signals (as for dispersed montmorillonite particles [64]). This research topic deserves careful attention in future.

The electrochemistry of vesicles

Present situation

Vesicles may be regarded as "soft matter particles" and have to be studied in suspensions because only there they possess properties which are relevant for their biological activity. Although vesicles may contain moieties possessing faradaic activity, normally they are constituted of molecules which will not be easily reducible or oxidizable. However, these molecules are rather hydrophobic, and thus, they have a great tendency to adsorb on hydrophobic electrodes, i.e., especially on mercury electrodes. Some years ago, we have discovered that liposomes suspended in aqueous electrolyte solutions undergo a complex destruction reaction on mercury electrodes; following a first interaction, they disintegrate and form an island of adsorbed lecithin molecules. This causes steep capacitive spikes on the ms time scale [65]. By integration of the capacitive spikes and modeling the resulting charge-time traces, it is possible to analyze the entire mechanism of liposome disintegration [66–71]. A wealth of quantitative data is accessible: the number of lecithin molecules per liposome, the size distribution of liposomes (measured as number of molecules per liposome), the phase transition temperature of membrane, the activation energy of the different steps of disintegration of liposomes, the overall rate of liposome disintegration (measured as number of disintegrating liposomes per time and surface area units), the rate of the different disintegration steps, and finally, the quantitative effect of membrane composition on all the before-mentioned data. We have expanded these studies to thrombocyte vesicles [72], reconstituted plasma membrane vesicles [73], and most recently, to mitochondria (Hermes et al., in preparation). In case of mitochondria, one can clearly determine the phase transition temperature, i.e., the temperature at which the membrane abruptly changes its adhesion-spreading properties, and one can also detect the effect of hypo-glycemic conditions during the cell growth before mitochondria separation.

Future perspectives

Since the adhesion-spreading studies of vesicles on mercury electrodes (which is the optimal choice, of course) reveal information on the membrane properties of the vesicles as well as size and composition related information, the present author sees various interesting future goals:

1. Very prosperous can be applications to cell organelles, like mitochondria, etc. Especially the study of the effects of chemicals (drugs, free radicals, nanoparticles, etc.) may yield important data for biology/medicine. Such studies should be extended to assess the effect of radical scavengers, or any other compounds interacting with the above-mentioned drugs and free radicals.
2. Possibly, the physiological state of cell organelles can be assessed by this technique.
3. Because the mechanism of vesicle adhesion-spreading on electrodes has much in common with vesicle fusion [48, 49], one can expect progress in understanding the fusion process, when these studies are extended.
4. The adhesion-spreading studies also lend themselves for assays of membrane activity of drugs, meaning here how they interact with the membrane and change its properties.

These are some linear extrapolations to the future, which can be easily written down considering the past and present state. Of course they cannot contain the unexpected discoveries, as those are usually made in the course of experimental and theoretical studies. Such discoveries may change the focus of future work and may put different questions in the centre. Exactly, this is what makes science so difficult to be planned. Our plans are extrapolations from the past and present, and while following these paths, we may discover new phenomena, and we may have new sparking ideas, from wherever they may come.

References

1. Scholz F, Lange B (1992) Trends Anal Chem 11:359–367

2. Scholz F, Meyer B (1994) Chem Soc Rev 23:341–347
3. Scholz F, Schröder U, Gulaboski R (2005) Electrochemistry of immobilized particles and droplets. Springer, Berlin
4. Oldham KB (1998) J Solid State Electrochem 2:367–377
5. Schröder U, Oldham KB, Myland JC, Mahon PJ, Scholz F (2000) J Solid State Electrochem 4:314–324
6. Komorsky-Lovrić Š, Mirčeski V, Kabbe Ch, Scholz F (2004) J Electroanal Chem 566:371–377
7. Bond AM, Marken F, Hill E, Compton RG, Hügel H (1997) J Chem Soc Perkin Trans 2:1735–1742
8. Bond AM, Fletcher S, Symons PG (1998) Analyst 123:1891–1904
9. Neufeld A (2003) Investigations using a Kelvin probe instrument and solid state electrochemical techniques: the initiation mechanism of corrosion of zinc and the solid-solid electrochemical transformation of CuTCNQ, PhD Thesis, Monash University, Melbourne
10. Neufeld AK, Madsen I, Bond AM, Hogan CF (2003) Chem Mater 15:3573–3585
11. Nafady A, Bond AM, Bilyk A (2008) J Phys Chem C 112:6700–6709
12. Doménech A, Doménech-Carbó MT, Vázquez de Agredos Pascual ML (2006) J Phys Chem B 110:6027–6039
13. Doménech A, Doménech-Carbó MT, Sánchez del Río M, Vázquez de Agredos Pascual ML, Lima E (2009) New J Chem 33:2371–2379
14. Doménech-Carbó A, Doménech-Carbó MT, Osete-Cortina L (2001) Electroanal 13:927–935
15. van Oorschot IHM, Grygar T, Dekkers MJ (2001) Earth Planet Sci Lett 193:631–642
16. Grygar T, Bezdicka P, Hradil D, Doménech-Carbo A, Marken F, Pikna L, Cepria G (2002) Analyst 127:1100–1107
17. Ramaraj R, Kabbe Ch, Scholz F (2000) Electrochem Commun 2:190–194
18. Keane L, Hogan C, Forster RJ (2002) Langmuir 18:4826–4833
19. Walsh DA, Keyes TE, Forster RJ (2002) J Electroanal Chem 538/539:75–85
20. Fay N, Dempsey E, Kennedy A, McCormac T (2003) J Electroanal Chem 556:63–74
21. Eklund JC, Bond AM (1999) J Amer Chem Soc 121:8306–8312
22. Perez-Ramirez J, Mul G, Kapteijn F, Moulijn JA, Overweg AR, Domenech A, Ribera A, Arends IWCE (2002) J Catal 207:113–126
23. Doménech A, Perez-Ramirez J, Ribera A, Mul G, Kapteijn F, Arends IWCE (2002) J Electroanal Chem 519:72–84
24. Doménech A, Alarcón J (2002) J Solid State Electrochem 6:443–450
25. Inzelt G (2002) J Solid State Electrochem 6:265–271
26. Inzelt G (2003) J Solid State Electrochem 7:503–510
27. Inzelt G, Puskás Z, Németh K, Varga I (2005) J Solid State Electrochem 9:823–835
28. Marken F, Webster RD, Bull St D, Davies St G (1997) J Electroanal Chem 437:209–218
29. Davies TJ, Brooks BA, Fisher AC, Yunus K, Wilkins AJ, Greene PR, Wadhawan JD, Compton RG (2003) J Phys Chem B 107:6431–6444
30. Scholz F, Komorsky-Lovrić Š, Lovrić M (2000) Electrochem Commun 2:112–118
31. Scholz F, Gulaboski R (2005) Chemphyschem 6:16–28
32. Scholz F (2006) Annu Rep Progr Chem Section C 102:43–70
33. Doménech A, Koshevoy IO, Montoya N, Pakkanen TA (2011) Electrochem Commun 13:96–98
34. Fiedler DA, Besenhard JO, Fooken MH (1997) J Power Sources 69:157–160
35. Dokko K, Horikoshi S, Itoh T, Nishizawa M, Abe T, Umeda M, Uchida I (2002) J Solid State Electrochem 6:188–193
36. Scholz F, Dostal A (1995) Angew Chem 107:2876–2878 (Angew Chem Int Ed Engl 34 (1995) 2685–2687)
37. Bárcena Soto M, Scholz F (2002) J Electroanal Chem 521:183–189
38. Widmann A, Kahlert H, Petrovic-Prelevic I, Wulff H, Yakhmi JV, Bagkar N, Scholz F (2002) Inorg Chem 42:5706–5715
39. Bond AM, Scholz F (1991) Langmuir 7:3197–3204
40. Meyer B, Zhang S, Scholz F (1996) Fresenius' J Anal Chem 356:267–270
41. Reddy SJ, Dostal A, Scholz F (1996) J Electroanal Chem 403:209–212
42. Scholz F, Lange B, Jaworski A, Pelzer J (1991) Fresenius J Anal Chem 340:140–144
43. Meyer B (1995) Entwicklung von festkörperelektrochemischen Methoden für die Mikroanalyse von Mineralen und synthetischen Festkörpern. PhD thesis, Humboldt-Universität, Berlin
44. Schröder U, Meyer B, Scholz F (1996) J Anal Chem 356:295–298
45. Suárez MF, Bond AM, Compton RG (1999) J Solid State Electrochem 4:24–33
46. Kucernak AR, Chowdhury PB, Wilde CP, Kelsall GH, Zhu YY, Williams DE (2000) Electrochim Acta 45:4483–4491
47. Hasse U, Wagner K, Scholz F (2004) J Solid State Electrochem 8:842–853
48. Hasse U, Fletcher S, Scholz F (2006) J Solid State Electrochem 10:833–840
49. Bárcena Soto M, Kubsch G, Scholz F (2002) J Electroanal Chem 528:18–26
50. Bárcena Soto M, Scholz F (2002) J Electroanal Chem 528:27–32
51. Lovric M, Scholz F (1997) J Solid State Electrochem 1:108–113
52. Lovric M, Hermes M, Scholz F (1998) J Solid State Electrochem 2:401–404
53. Lovric M, Scholz F (1999) J Solid State Electrochem 3:172–175
54. Myland JC, Oldham KB (2000) Electrochem Commun 2:541–546
55. Hasse U, Scholz F (2001) Electrochem Commun 3:429–434
56. Lovric M, Hermes M, Scholz F (2000) J Solid State Electrochem 4:394–401
57. Takeda N, Stawasz ME, Parkinson BA (2001) J Electroanal Chem 498:19–33
58. Komorsky-Lovric Š, Scholz F (1998) J Electroanal Chem 445:81–87
59. Ura H, Nishina T, Uchida I (1995) J Electroanal Chem 396:169–173
60. Uchida I, Fujiyoshi H, Waki S (1997) J Power Sources 68:139–144
61. Perdicakis M, Grosselin N, Bessière J (1997) Electrochim Acta 42:3351–3358
62. Hasse U, Scholz F (2004) Electrochem Commun 6:409–412
63. Hasse U, Scholz F (2005) Electrochem Commun 7:173–176
64. Scholz F, Hellberg D, Harnisch F, Hummel A, Hasse U (2004) Electrochem Commun 6:929–933
65. Hellberg D, Scholz F, Schauer F, Weitschies W (2002) Electrochem Commun 4:305–309
66. Hellberg D, Scholz F, Schubert F, Lovrić M, Omanović D, Agmo Hernández V, Thede R (2005) J Phys Chem B 109:14715–14726
67. Agmo Hernández V, Scholz F (2006) Langmuir 22:10723–10731
68. Agmo Hernández V, Scholz F (2008) Isr J Chem 48:169–184
69. Agmo Hernández V, Scholz F (2008) Bioelectrochemistry 74:149–156
70. Agmo Hernández V, Hermes M, Milchev A, Scholz F (2009) J Solid State Electrochem 13:639–649
71. Agmo Hernández V, Milchev A, Scholz FJ (2009) J Solid State Electrochem 13:1111–1114
72. Agmo Hernández V, Niessen J, Harnisch F, Block S, Greinacher A, Kroemer HK, Helm CA, Scholz F (2008) Bioelectrochemistry 74:210–216
73. Czesnick C (2010) Nitric oxide effects on liposomes and plant plasma membranes. Diploma thesis, University of Greifswald