Electroanalytical chemistry for the analysis of solids: Characterization and classification (IUPAC Technical Report)*

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Abstract: Solid state electroanalytical chemistry (SSEAC) deals with studies of the processes, materials, and methods specifically aimed to obtain analytical information (quantitative elemental composition, phase composition, structure information, and reactivity) on solid materials by means of electrochemical methods. The electrochemical characterization of solids is not only crucial for electrochemical applications of materials (e.g., in batteries, fuel cells, corrosion protection, electrochemical machining, etc.) but it lends itself also for providing analytical information on the structure and chemical and mineralogical composition of solid materials of all kinds such as metals and alloys, various films, conducting polymers, and materials used in nanotechnology. The present report concerns the relationships between molecular electrochemistry (i.e., solution electrochemistry) and solid state electrochemistry as applied to analysis. Special attention is focused on a critical evaluation of the different types of analytical information that are accessible by SSEAC.

Keywords: analytical chemistry; chemical analysis; electrochemistry; IUPAC Analytical Chemistry Division; solids.

CONTENT

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1. INTRODUCTION

The aim of the current technical report is to characterize, classify, and evaluate critically the present state of the art of studies of the processes, materials, and methods specifically aimed to obtain analytical information (quantitative elemental composition, phase composition, structure information, and reactivity) on solid materials by means of electrochemical methods. This field is described here by the term "solid state electroanalytical chemistry" (SSEAC). Definitions and recommendations for terminology and usage of symbols in electrochemistry [1] and, more specifically, in electroanalytical chemistry [2–4] have been previously provided by IUPAC and are accepted within this report.

The electrochemical characterization of solids is not only very valuable for electrochemical applications of materials (e.g., in batteries, fuel cells, corrosion protection, electrochemical machining, etc.) but it lends itself also for providing analytical information on the structure and chemical and mineralogical composition of solid materials of various kinds, e.g., metals and alloys, films in electrochemical biosensors [5,6], conducting polymers, and materials used in nanotechnology (redox-active nanomaterials, catalyst nanocomposites, metallic nanoparticles, etc.) [7].

In agreement with the definition of electrochemistry as "the science of structures and processes at and through the interface between an electronic ('electrode') and an ionic conductor ('electrolyte') or between two ionic conductors" [8,9], one can distinguish between solution, solid state, and plasma electrochemistry according to the studied objects [10]. In a very narrow sense, solid state electrochemistry refers to electrochemical systems where (at least) one solid ionic conductor is involved. In a wider meaning, however, solid state electrochemistry comprises all electrochemistry in which at least one solid phase plays a *decisive* role. This is the philosophy adapted by the editors of the *Journal of Solid State Electrochemistry* [11].

This report is focused on all aspects of solid state electrochemistry dealing with the analysis of solid materials forming the working electrode or distributed on the surface of an electron-conducting electrode in contact with a suitable liquid electrolyte. In the latter case, the electrode, which is usually solid [graphite, indium-doped tin oxide (ITO), fluorine-doped tin oxide (FTO), Au, Pt, etc.], but sometimes also liquid (Hg), is termed the "base electrode" while the solid material being investigated is considered as the "analyte(s)". Following previous technical reports [2–4], the working electrode is an electrode that serves as a transducer responding to the excitation signal and the concentration of the substance of interest in the solution being investigated, and that permits the flow of current sufficiently large to effect appreciable changes of bulk composition within the ordinary duration of a measurement [3,4]. In electroanalytical chemistry for the analysis of solids (i.e., SSEAC) the material to be investigated can form the working electrode itself or can be anchored to a base electrode. The term "base electrode" is applied to an electron conductor to which the solid material under investigation is attached or embedded, as to form conjointly the working electrode. The attachment can be made by means of adsorption (e.g., riboflavine on glassy carbon), mechanical transfer, embedding into a carbon paste, polymer, etc., chemical or electrochemical precipitation, covalent bonding, etc. The resulting working electrode is referred to as a (chemically) modified (base) electrode [12,13].

> *Note*:   The mechanical attachment/transfer represents a rather specific way of modifying the base electrode. Here, the chemical modifier is mechanically transferred by means of abrasion [14] or by evaporation of the volatile liquid phase of a suspension [15], to the surface of a solid electrode, often paraffin-impregnated graphite rods, forming a surface-modified electrode. Resulting modified electrode can be applied as an ion-selective potentiometric sensor, and also for amperometric and voltammetric sensing.

Following previous technical reports [12], a chemically modified electrode (CME) i**s** an electrode made of a conducting or semiconducting material that is coated with a selected monomolecular, multi-molecular, ionic, or polymeric film of a chemical modifier and that by means of faradaic (charge-transfer) reactions or interfacial potential differences (no net charge transfer) exhibits chemical, electrochemical, and/or optical properties of the film. The term "film" is used here in its meaning of a generic term referring to condensed matter restricted in one dimension [20]. Compared to other electrode concepts in electrochemistry, the distinguishing feature of a CME is that generally a quite thin film (from a molecular monolayer to perhaps a few micrometers-thick multilayer) of a selected chemical is bonded to or coated on the electrode surface to endow the electrode with the chemical, electrochemical, optical, electrical, transport, and other desirable properties of the film in a rational, chemically designed manner.

In agreement with Bond and Scholz [16], the term "surface-modified electrode" (SME) should be/is applied strictly to electrodes which have been altered by coating the electrode surface with a thin film of a specified material so as to introduce a specific reaction or response. In general, SMEs are prepared in order to enhance the analytical performance (increasing sensitivity, selectivity, or both) of the electrode with respect to an analyte (or a family of analytes) in solution so that the SME acts as a potentiometric, conductometric (impedimetric), amperometric, or voltammetric sensor. Electrode modification can be carried out by means of a variety of procedures while the electrode configuration can involve structures from monomolecular layers to multi-layers having a more or less complicated architecture at the nanoscopic level. Chemically modified carbon paste electrodes, although not being SMEs *sensu stricto*, because the modifier is not distributed in a thin film on the electrode surface, can be included within the SMEs [16].

In this sense, electrodes used in SSEAC can also be considered as SMEs. Two distinctive aspects, however, characterize modified electrodes used in SSEAC: (i) the electrode modification is performed in order to obtain analytical information on the *electrode modifier* rather than on an analyte in the electrolyte solution; (ii) the mechanically attached solids do not form necessarily true/compact thin films as it is considered by the definition of a CME [12]. In fact, a non-uniform distribution (non-homogeneous due to the particulate nature) of the solid chemical modifier can be seen as a specific feature of that kind of working electrodes in SSEAC. Obtaining analytical information on solids using electrochemical methods implies that such methods are applied as a part of an analytical process which is, in principle, motivated by social demands (such as environmental pollution monitoring) resulting in specific analytical demands (such as increase in sensitivity and selectivity, accuracy and precision of results, and complexity of analytical information), as emphasized by Bard [17].

Note: The terms associated with electrochemistry as a principle of measurement and those associated with measurement methods and procedures are reported in previous technical recommendations [18–20]. With regard to analytical chemistry, the position of the SSEAC approach can be viewed within a hierarchical relation between different concepts involved in chemical analysis [21–23]. The analyte is regarded here in a wide meaning as the chemical species whose presence, abundance, structure, and/or distribution in the solid material is investigated. The analyte can be either the solid material itself (e.g., lead sulfide) or one of the components of the solid material at the atomic-molecular level (e.g., iron ions in Fe-ZSM5-zeolites). Notice that analyte is not equivalent to measurand [18].

It should be recognized that there is a transition from "molecular electrochemistry" to "solid state electrochemistry" according to the size of the entities involved in interfacial charge-transfer processes (and the level of attachment to the base electrode). A possible scheme illustrating the relationships between different topics involved in the transition from molecular electrochemistry to solid state electrochemistry is given in Fig. 1. The scope of molecular electrochemistry was discussed in a previous technical report by Savéant [24].
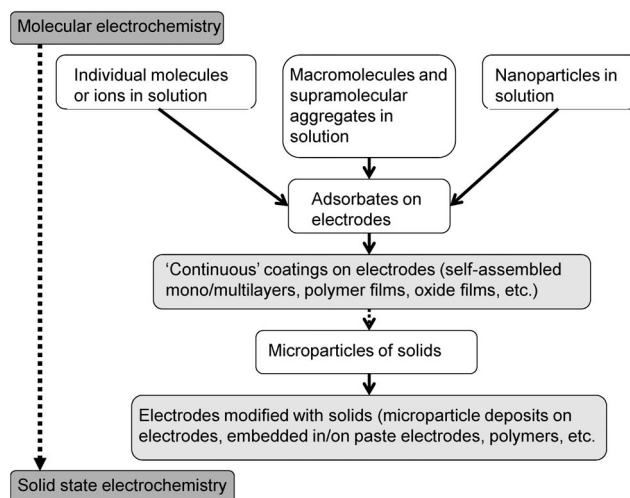
Fig. 1 Scheme of possible relationships among topics typically involved in the transition from molecular electrochemistry to solid state electrochemistry.

Strictly taken, SSEAC involves only systems where the material to be analyzed is of genuine solid nature and forms the electrode or is deposited on a base electrode. These systems include:

- solid inorganic compounds (typically, metal oxides, sulfides, halides, metal complexes, poly-oxometalates, organometallic compounds, minerals, etc.), including doped materials and solid solutions;
- solid metals and alloys, semiconductors;
- solid organic compounds including natural products or mixtures of products;
- micro- and mesoporous materials with or without electroactive guest ions or molecules (functionalized zeolites, hydrotalcites, silica, silicates, etc.); and
- metal–organic frameworks and related materials exhibiting high permeability to ion transfer often referred to as ionic sponges.

> *Note*:   Systems such as adsorbates of proteins, biopolymers, self-assembled mono-layers/multi-layers, Langmuir–Blodgett films, and polymeric films prepared by chemical or electrochemical deposition (including redox polymers, conducting polymers, etc.) can be considered to be at the boundary between solid state and molecular electrochemistry. Most of these systems are increasingly used in electrochemical sensing combined with genuine solid materials to form composites (e.g., conducting polymers + zeolite composites) or functionalized materials (with different types of functionalization, from adsorption to covalent attachment) and/or "hybrid" materials so that a wide variety of systems is available (e.g., Au nanoparticles on TiO_2) forming different "supramolecular architectures". Such systems will be treated here only as far as their composition is able to be investigated by means of SSEAC methodologies.

Coatings by polymer films and composites are extensively studied because of their electrochemical and, in particular, electroanalytical applications. Reviews on conducting polymers [25–27] and nanocomposites with metal nanoparticles [7] and carbon nanotubes [28–30] are available.

> *Note*:   SSEAC methods provide different electrochemical responses for different minerals having the same chemical composition, for instance, identification of different mineral species (e.g., hematite, α-Fe_2O_3, and maghemite, γ-Fe_2O_3) having the same chemical

composition, is possible [31]. For this reason, mineralogical terms rather than chemical nomenclature have often been used in the text.

2. ELECTROCHEMICAL METHODS FOR THE ANALYSIS OF SOLIDS

Electrography, developed by Fritz [32] and Glazunov [33], extended by Weisz [34] and others [31], is an early application of electrochemical methods to identify solid samples. Only in the 1960s, with the introduction of carbon paste electrodes by Adams [35] and Kuwana et al. [36,37], the analysis of solids by means of electrochemical methods received more attention. In the 1970s and 1980s, the carbon paste electrodes with both electrolyte and non-electrolyte binders were increasingly used, particularly for mineral analysis by Bauer et al. [38], Songina et al. [39–41], Brainina et al. [42,43], Zakharchuk [44,45], and many others. From the late 1980s, the introduction of the voltammetry of immobilized particles (VIMP) by Scholz et al. [31,46–49] has expanded the scope of the application of solid state electrochemistry for the analysis of solids to a variety of fields [50–57], mainly because the limitations of the previously developed techniques with respect to accessible materials could be overcome. Parallel to the experimental research, the theoretical modelling of the electrochemical processes of solid particles was developed [35,36,53,54,58–83]. Research in this field has experienced a continuous growth from the late 1980s, as illustrated in Fig. 2, where the cumulative number of indexed publications (Scopus index) is depicted.
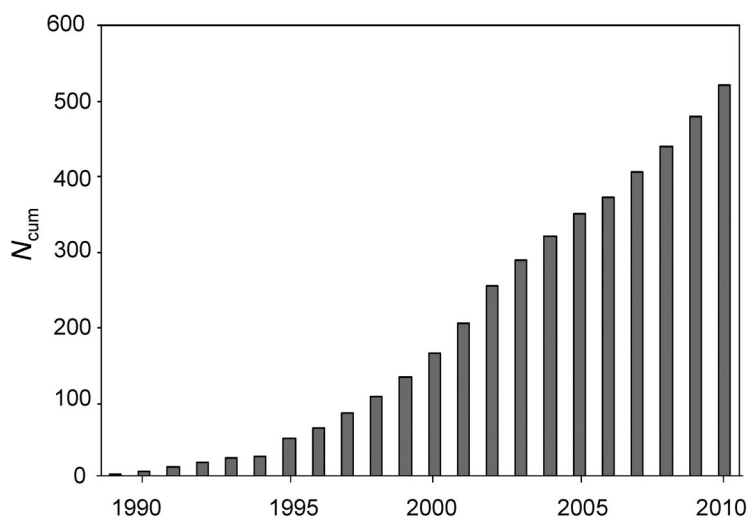

Fig. 2 Cumulative number of indexed articles, N_{cum}, dealing with the VIMP in the period 1989–2010.

2.1 Types of cells

Two basic types of electrochemical cells have been used in SSEAC: (a) pressed and sandwiched two-electrode cells or pressed graphite-material pellets, based on powdering and mixing the material to be analyzed with graphite powder and pressing the powder mixture between planar electrodes [84], and (b) three-electrode cells with solid-modified electrodes in contact with a liquid electrolyte. Different alternatives for local analysis of metals and alloys using portable cells are possible [85–87]. In several cases, the solid to be investigated is present in suspension in the electrolyte [88,89].

2.2 Preparation of electrodes

Various approaches are typically utilized to prepare the working electrode:

- Direct deposition of microparticulate deposits of solids from a suspension. Here, a drop of a suspension of the solid in a volatile liquid is placed on the surface of the basal electrode and the solvent is allowed or forced to evaporate [90].
- Embedding the solid into a polymer coating from a suspension of the solid in a solution of the polymer in a volatile solvent [91] or covering a microparticulate deposit of the solid by a polymer layer [92].
- Embedding the solid into a carbon paste electrode (CPE) [35–45]. Here, the solid used as an electrode modifier can be attached either to the surface, or it is embedded in the bulk phase of the paste (see note below).
- Composite electrodes. Rigid composite electrodes can be prepared by mixing the solid with graphite powder, a monomer, and a cross-linking agent, followed by radical-initiated copolymerization [93].
- Microparticulate deposits formed by mechanical transfer of the solid on an inert electrode [46–49]. The mechanical (sometimes abrasive) transfer of microparticles of solids to the surface of an inert electrode, typically a paraffin-impregnated graphite electrode ensures a direct exposure of the particle surface and the particle/electrode junction to the electrolyte. This is the key approach used in VIMP methodology. Boron-doped diamond electrodes [94], lead pencil electrodes [95], ITO electrodes [96], and metal electrodes [97] have been also used.
- Solid electrodes made of the material under investigation, e.g., for the analysis of minerals with semiconducting properties, typically magnetite [98–100] and galena [101–103]. Usually, the electrodes consisted of bars of the studied material housed in a Teflon shaft.

  Note: Chemically modified CPEs have been extensively used to analyze solid materials. As described in comprehensive reviews [104–107], two types of CPEs, using electrolyte and non-electrolyte binders, are used. In CPEs with non-electrolyte binders, a small amount of the solid analyte is mixed with graphite powder to make a paste. In this case, the electron-transfer processes occur at the paste–electrolyte interface, so that the particle size distribution, the nature of the binder, and paste composition affect the electrochemical response. A variety of carbon-based materials have been introduced recently. These include glassy carbon powder [108], acetylene black [109], template carbon or porous carbon foam [110], doped diamond [111], fullerenes [112], carbon nanofibres [113], and nanotubes [114]. The scope of CPEs has been significantly expanded by the use of ionic liquids [115] or binding agents, like phenantrene, undergoing solidification during carbon paste preparation [116]. Carbon inks and screen-printed carbon electrodes are directly related [117]. Carbon composite electrodes using polymeric binders have also been used [118,119].

  Note: A growing number of methods to prepare solid-modified electrodes has been developed during the last decades. These include, among others, spin coating and formation of Langmuir–Blodgett films, self-assembled monolayer formation, layer-by-layer deposition, electrophoretic deposition, hydrothermal crystallization on conductive substrates, and formation of solid coatings by anodic growth on metal surfaces [56]. These methodologies, which are typically used for electrode modification aimed at analyzing species in solution rather than analyzing solids, will not be treated here.

2.3 Electrochemical techniques/methods

Obtaining the electrochemical response of non-conducting solid materials requires their direct contact with an electron-conducting electrode or their dispersion into a conducting matrix. Dynamic interfacial electroanalytical techniques are by far the most frequently used in SSEAC [12,34,50–53]. In particular, cyclic voltammetry and linear potential scan voltammetry are in the first place, followed by differential pulse and square-wave voltammetry. These techniques are complemented by chronocoulometry [120], chronoamperometry [61], chronopotentiometry [121], electrochemical impedance spectroscopy (EIS), electrochemical noise (EN) analysis [122], and electrochemical quartz crystal microbalance (EQCM) measurements [123–126]. All these techniques are available with conventional electrochemical equipment.

The scope of available electrochemical techniques has been recently extended in two directions:

(a) Introducing techniques based on measurements at the nanoscopic domain: scanning electrochemical microscopy (SECM) [127–130] and electrochemical scanning tunnelling microscopy [131].
(b) Hyphenating electrochemical with non-electrochemical techniques to perform in situ monitoring of solid state reactions. Examples of the hyphenated non-electrochemical techniques are: X-ray diffraction [132], microscopy, spectroelectrochemistry and diffuse reflectance spectroscopy [133–135], atomic force microscopy [136–139], electron spin resonance [140], and thermal analysis [141,142].

3. ELECTROCHEMICAL PROCESSES AND THEORETICAL MODELING

Solid phases are directly involved in various electrochemical processes, for instance:

(a) electrodeposition of metals and other solid materials from solutions;
(b) reductive/oxidative dissolution of solids [e.g., reductive dissolution of Fe(III)-oxides and oxide hydrates, oxidative dissolution of chromium oxide];
(c) electrochemical generation and growth of compounds on the electrode surface, for instance, anodic formation of protective metal oxide films;
(d) electrochemical (and also photoelectrochemical, etc.) transformations of conducting/semi-conducting solids acting as electrodes in contact with liquid electrolytes (or also in contact with liquid or gaseous non-electrolytes).
(e) electrochemically initiated chemical transformations, such as isomerizations, etc.; and
(f) electrochemical transformations of solids mechanically immobilized on electrodes. These transformations may belong to (a) to (e).

Although most of these processes can be used to obtain analytical information on solids, we like to define SSEAC in such way as to restrict it to applications where electrochemical reactions of solid materials forming electrodes or attached to inert electrodes are used deliberately for the sake of obtaining analytical information.

Theoretical modeling has been developed with respect to a series of phenomena. A non-exhaustive list includes:

- propagation of an electrochemical transformation through microcrystals [62];
- initiation of the electrochemical reaction at the three-phase electrode/particle/electrolyte boundary [60];
- advancement of reaction fronts in insertion electrochemistry of single particles immobilized on electrodes [69];
- role of the three-phase junction in the electrochemistry of immobilized insulator particles [66];

- effect of electrolyte concentration on insertion electrochemistry of single particles immobilized on electrodes [67];
- effect of miscibility gaps in insertion electrochemistry of single particles immobilized on electrodes [63,70];
- charge diffusion on the surface of immobilized spherical particles [75,76];
- voltammetry at random microparticle arrays [72,73,78];
- dissolution of microparticle arrays [72];
- irreversible electrochemical stripping of microparticles [42,43,82,83]; and
- irreversible reductive or oxidative dissolution of metal oxides and related materials [61,64,65].

> *Comment*: In this context, the terms "ion insertion" and "ion expulsion" denote the exchange of electrolyte counterions between the solid and the solution when electrochemical reactions proceed. The terms "doping" and "de-doping" are frequently used for these processes; however, this should be discouraged because "doping" is used in semiconductor sciences in the sense of adding minority species. Also, the term "ion trapping" should be discouraged as "trapping" tends to imply irreversibility (although this can indeed sometimes be observed). The term "ion encapsulation" (and also "molecule encapsulation") can be applied in cases where an ion (or molecule) is anchored within the cavities of molecular dimensions created by the solid framework. Then, the encapsulated ion or molecule is the guest species in the host solid lattice. In most cases, there is an intermediate situation where the guest species are located in more or less external positions of a solid framework, which exhibits a more or less complicated topology, for instance, in layered hydroxides, functionalized silicas and aluminosilicates, and polyoxometallates [130].

> *Comment*: As required by charge conservation, solid-to-solid transformations involve the exchange of ions between the electrolyte and the solid material. In general, for a solid material containing mobile ions, a reduction process can occur either via the ingress of a cation from the electrolyte into the solid material or the expulsion of an anion from the solid to the electrolyte, coupled with the electron transfer, whereas an oxidation process requires either the ingress of an anion from the electrolyte or the expulsion of a cation from the solid. Such processes are nonequivalent, as studied by Bond et al. for the electrochemical oxidation of microcrystals of $[(C_4H_9)_4N][(CO)_5CrI]$ mechanically attached to a gold electrode [130].

> *Note*: There is a possibility that the guest species occupy different positions in the solid framework, i.e., they may be adsorbed on the surface or housed in the voids, channels, and cavities of the lattice. Apart from this, reticular defects (dislocations and crevices, etc.) can influence the electrochemical response in general by increasing the accessibility of the guest species to the charge-transfer processes. The term "topological redox isomers" [143,144] is attributed to species occupying different positions in the host solid framework. Additionally, there is the possibility of different coexisting species in the same solid framework, for instance, nanoparticulate iron oxides accompanied by intra- and extra-framework iron ions in Fe–ZSM5 zeolites [145,146].

4. ANALYSIS OF SOLIDS BY SOLID STATE ELECTROCHEMISTRY

There are a variety of elements, compounds, and materials that can be identified (qualitative analysis, phase designation) by solid state electrochemistry techniques, and in many cases their quantitative composition can also be determined by these techniques. These include, among others, minerals (metal oxides, halides, sulfides, etc.); metals and alloys; various synthetic products such as magnetic and superconducting materials; solid solutions (alloys, nonstoichiometric oxides, sulfides, doped metal

oxides, and related compounds, etc.); metal complexes and organometallic compounds; polycyano-metalates; polyoxometalates; metal phthalocyanines; metal carbonyl compounds; organic compounds, including natural compounds, zeolites, and other micro- and mesoporous silicates and aluminosilicates containing cationic and anionic electroactive guests, fullerenes, and other "carbons"; and layered hydroxides and related materials, including composites with polymers, metal–organic frameworks, glass, and glazed and ceramic materials [31,50–56,147].

4.1 Types of analytical information

Potentially, SSEAC can provide three different kinds of information about solids: (A) the element composition (qualitative and quantitative), (B) information on the redox state of electroactive elements, and (C) the phase composition (also with respect to qualitative phase identification and with respect to a quantification of phases).

(A)   The electrochemically active elements of a solid compound can be *qualitatively identified*. Example: the elements Bi, Cu, and Pb can be identified in $Bi_{1.8}Pb_{0.39}Sr_{1.99}Ca_{2.06}Cu_{3.15}O_{l0.5}$, and the relative amounts of these three electroactive elements can be *quantified* [148].

(B)   Identification and relative quantification of the redox state; for instance, Fe(III) and Fe(II) species in clays and ceramic materials [149].

(C)   A phase mixture can be unambiguously distinguished from a single solid solution phase, and phase mixtures can be quantitatively analyzed. Example: see below the identification of the two phases CuS and CuSe, and the quantitative analysis of the solid solutions $CuSe_{1-x}S_x$ [150].

Of course, SSEAC cannot provide structure information on an absolute basis, like X-ray diffraction, and all information has to be derived on a fingerprint basis following collecting of the "spectra" of pure phases, or, as in the case of solid solutions, on the basis of the rules of mixed-phase thermodynamics.

Figure 3 shows a possible scheme for the main types of analytical information attainable by SSEAC. Identification of simple phases involves, for instance, mineralogical identification or pigment identification and quantification in samples containing, for instance, mixtures of minerals or pigments
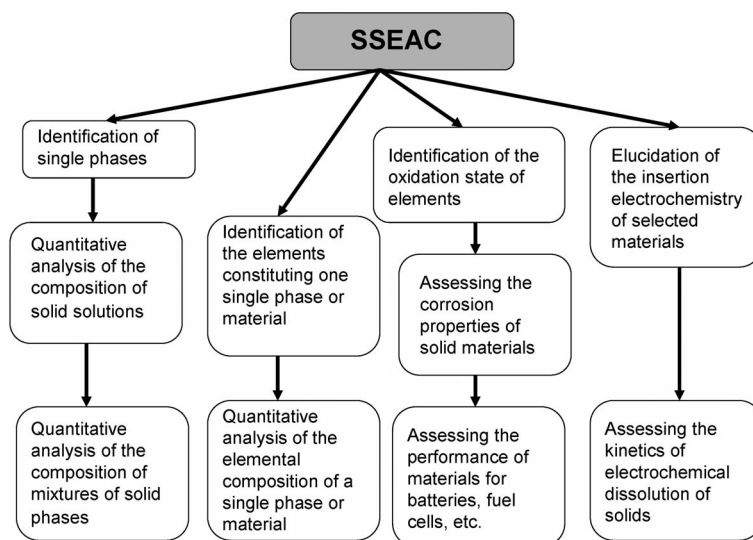

Fig. 3 Scheme of the relationships among the types of analytical information provided using SSEAC.

immersed into binding media. Identification and quantification of elements existing in a simple phase implies, for instance, the analysis of impurities of a given "foreign" element in a mineral, dopants in semiconductors, etc.

This analytical information can be also applied in studies on metal corrosion/protection (identification of corrosion products, anodic growth of metal oxides on metal surfaces, etc.) on electrotechnical materials for batteries, supercapacitors, and fuel cells (energetic performance, cycleability, etc.), which will not be treated here.

Note: The application of solid state electrochemistry is, however, extended to the determination of physico-chemical properties of solids and solutions. Solid state voltammetric techniques permit determination of the thermodynamic properties of compounds [150] and individual guest species entrapped into microporous solid systems [144,151]. Recent approaches involve measurement of individual Gibbs free energies of anion [153] and cation [154] transfer between two solvents. The study of size selectivity and the determination of diffusion coefficients for electrons and ions in solid materials can also be obtained from solid state electrochemical experiments [155]; in particular, for processes involving cation [156,157] and anion [158] diffusion in micro- and mesoporous aluminosilicates, as well as metal–organic frameworks [159,160]. Electron transfer coupled to proton transfer has been studied for organometallic compounds [161], polyoxometallates [162], and organic compounds [163,164].

Additionally, SSEAC methods provide information on the reactivity of solid compounds, both from a thermodynamic as well as from a kinetic point of view. Available examples include nucleation, growth, redistribution, and dissolution processes in fullerenes [165] and metal–organic frameworks [159,160], electrochemical lattice reconstruction in hexacyanometallates [166], electron self-exchange in the solid state [167], and formation of solid inclusion complexes [168].

4.2 Qualitative analysis

"Qualitative analysis" is used here in the sense of "identification" of chemical species, for instance, elements, redox centres, compounds, and phases. The sample can consist of a single compound (or phase), or it may be a mixture of compounds (phases). Most frequently, voltammetric techniques are used for this purpose. In the direct approach, the analyte(s) is/are identified by means of its/their specific voltammetric response obtained, under fixed electrochemical conditions, in a suitable electrolyte. It is pertinent to note:

• Solid state electroanalytical techniques (VIMP in particular) permit one to distinguish and identify different crystalline forms of a given mineral or compound (and/or identifying and distinguishing different minerals) [46–54].
• In several applications, the analyte is a natural product, not necessarily a pure compound, associated with other components which form a more or less complex system. This is the case when inorganic and organic pigments are identified in paintings [55].
• The analytes can also be individual species located in a matrix such as pigmenting ions in glass materials [55] or guest molecules and ions in microporous solids [56].

In most cases, the sample to be analyzed involves mixtures of compounds which, in favourable cases, can be resolved. This is the case shown in Fig. 4, corresponding to the square-wave voltammetry of a sample from the "La Trasfigurazione" wall painting in the Borgherini Chapel of the Sant Pietro in Montorio church in Rome, painted by Sebastiano del Piombo in 1521–1524: The voltammogram of the paint sample fits well with the sum of those recorded for azurite and lead white independently, thus suggesting that the sample contains a mixture of these pigments.
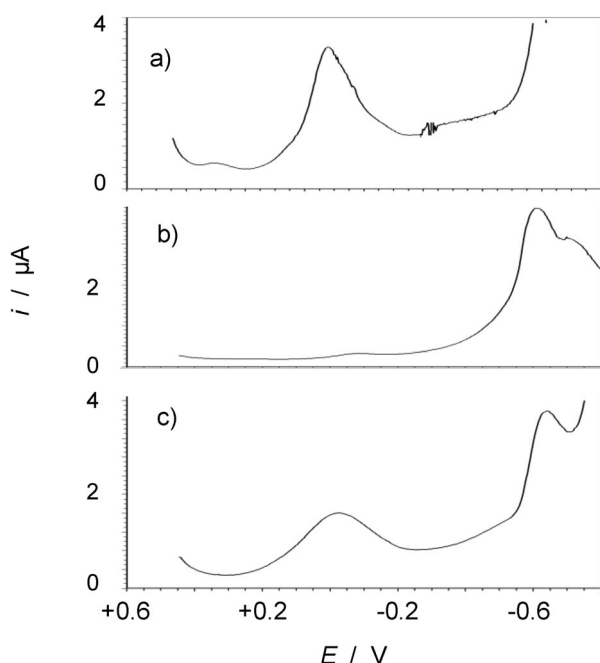
Fig. 4 Square-wave voltammograms of ca. 0.1 μg samples of (a) azurite, (b) lead white, and (c) sample from the "La Trasfigurazione" wall painting in the Sant Pietro in Montorio church in Rome, attached to paraffin-impregnated graphite electrodes in contact with aqueous 0.485 mol kg^{-1} sodium acetate buffered solution, pH 4.85, Ag/AgCl (3 mol dm^{-3} NaCl) reference electrode. (A. Doménech and M. T. Doménech, unpublished results; conditions such as in ref. [181]).

Alternatively (or complementarily), analytical information can be derived from studies of the catalytic [169–172] and photoelectrocatalytic [173] effects of selected electrochemical processes. This involves the use of a redox probe in the electrolyte able to be catalyzed by the analyte, as previously mentioned.

Note: A mineral can be identified in a first examination based on the characteristic potentials (e.g., peak potentials) of mineral-specific signals under fixed chemical and electrochemical conditions (electrolyte, electrode conditioning, electrochemical parameters). However, the peak potential and the peak profile are also dependent on the shape and size distribution of the microparticulate deposit on the electrode. The degree of hydration and crystallinity of the solid can also significantly affect the observed voltammetric response while possible electroactive species in the sample may interfere in the analyte identification. Then, electrochemical identification of solid analytes (or analytes in solids) should involve the use of different analytical strategies (vide infra) and the use of shape-dependent parameters other than peak potentials for identification purposes.

4.3 Quantitative analysis

Quantification of constituents of solid samples by SSEAC is possible on the basis of coulometry and voltammetry. The determination of absolute mass fraction; i.e., the mass of constituent divided by the mass of the solid sample, of a given constituent in a solid sample is not an easy task, and so far that task has been solved only with the help of an inner standard (see below). In the context of SSEAC, an inner

standard is a solid material (preferably an element or compound) exhibiting a well-defined solid state electrochemical response that is added to the sample in known proportion so that it produces a signal able to be measured separately from those of the components of the sample. For a direct determination of an absolute mass fraction (without using an inner standard) it would be necessary to transfer a known amount of sample to the electrode surface, and one has to make sure that this amount stays there and can be completely transformed in the electrochemical reaction used for analysis. Clearly, this approach fails already for the transfer of a known amount. There is no balance with which the amounts used in VIMP could be measured (EQCM may be applicable in some cases, but nothing has been published yet on a combination of EQCM with VIMP for the sake of quantitative analysis).

The relative quantification of constituents (the molar and/or mass ratio of different electroactive components) of solids by SSEAC is possible applying different chronocoulometric and voltammetric approaches. An example is the determination of the ratio of thallium to tin in various thallium-tin sulfides [174]. The transferred sulfide is reduced using an electrolyte solution that contains mercury ions. Similar to what happens in case of thin-mercury film electrodes, the deposited mercury dissolves the tin and the thallium, and the oxidation of the two metals can be recorded by chronocoulometry so that the ratio can be calculated. Another example is the determination of the oxidation state of sulfur in different thallium sulfides [174]: That method is based on measuring in a first step the charge consumed for reduction of the thallium sulfide to thallium, and in a following step the determination of the charge of oxidation of the thallium metal. The metal ratios of high-temperature superconductors have also been determined by SSEAC [175]. The ratios of the constituents of alloys can be easily determined based on the oxidation signals of the single constituents [46–54]. Calibration curves must be used because the relations between the ratios of peak currents of constituents and composition are strongly nonlinear and not predictable by any theory [176].

The constituents of powder mixtures can be analyzed with SSEAC when the constituents possess individual signals which do not interfere (or simply overlap) with each other [177]. Also in the case of powder mixtures, it is necessary to use calibration graphs "ratio of peak currents vs. composition". These calibration graphs are nonlinear even when the underlying dependencies "peak current vs. absolute concentration" are linear [177].

In case of *solid solutions*, a very elegant possibility exists because of the dependence of characteristic potentials (peak potentials) on composition [152,178]. As an example, we may refer to the solid solutions of CuS and CuSe: whereas both compounds give specific and well-separated reduction signals, the solid solutions of these compounds possess only one signal that shifts from the value of CuS to that of CuSe when the composition of the solid solutions is varied (see Fig. 5).

The reason for this is the thermodynamics of solid solutions (mixed-phase thermodynamics). For ideal solid solutions, the function of peak potential vs. molar ratio is slightly nonlinear for reasons of mixing entropy. In real cases, the deviations may be rather large (see Fig. 6) [152]. It is interesting that even for completely irreversible systems, such analyses can be performed. Examples are solid solutions of iron and manganese oxides [179,180]. The specific properties of solid solutions allow a very simple distinguishing between "solid solutions" and "phase mixtures", a task of high importance in materials science. Figure 4 already provides one impressive example of how these two cases can be easily identified, and Fig. 7 gives another example.

In the case of a sample containing two (or more) electroactive species, X and Y, displaying well-resolved electrochemical signals whose magnitude (e.g., peak current i) i_X, i_Y, can be taken as proportional to the mole number and, equivalently, the mass of the corresponding component, m_X, m_Y, the amount of the component Y relative to that of the component X can be obtained, simply as the i_Y/i_X ratio; i.e., $m_Y/m_X \propto i_Y/i_X$. Of course, this relation will usually be non-linear.

In the case of strongly overlapping signals, a method has been reported for the relative quantification of components based on the Tafel analysis of voltammograms [181] using measured currents, i, and potentials, E, of the rising part of voltammetric peaks. This is the case of copper pigments for which peak potentials for reductive processes in contact with aqueous electrolytes are quite similar. Under the
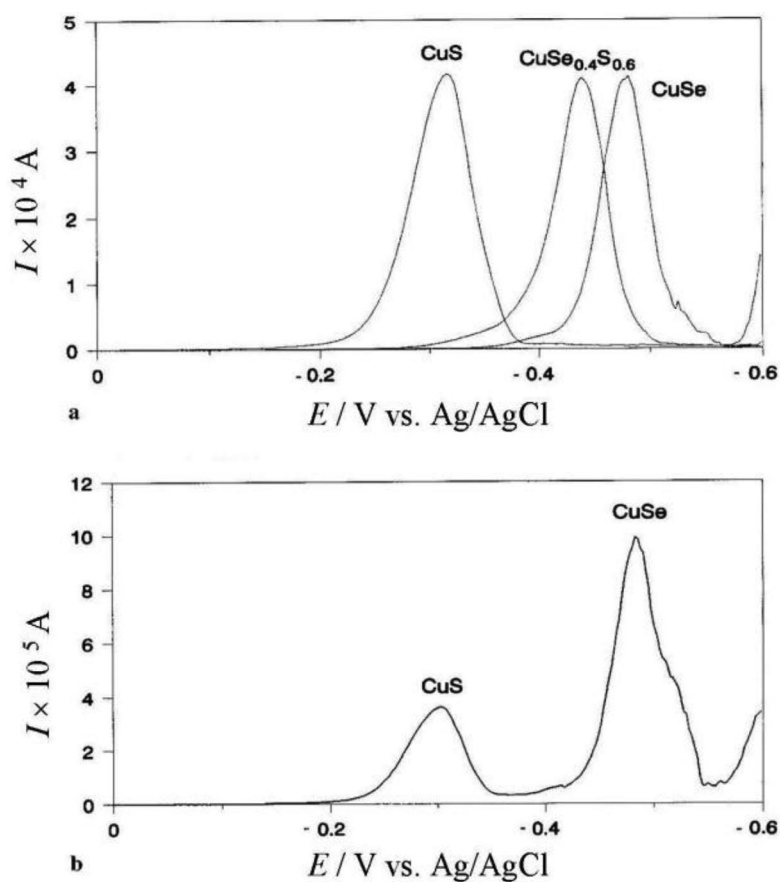
Fig. 5 (a) Three individual linear potential scan voltammograms of the reduction of the pure phases CuS and CuSe, and the solid solution $CuSe_{0.4}S_{0.6}$. (b) Voltammogram of the powder mixture of the pure phases CuS and CuSe. Reproduced from [152], with permission.

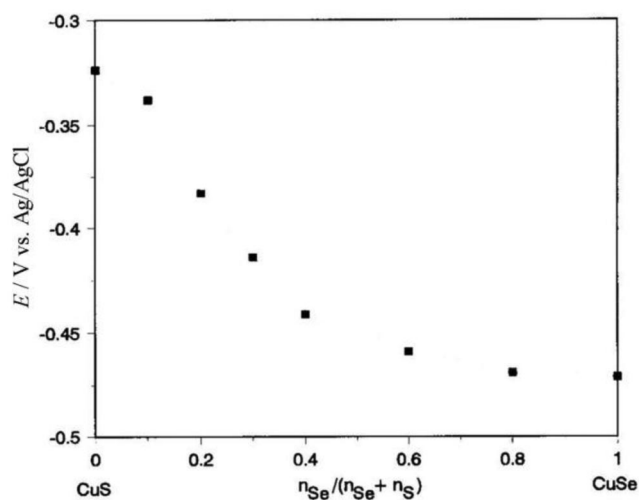**Fig. 6** Dependence of the peak potential on composition of the solid CuS_xSe_{1-x} solutions. Reproduced from [152], with permission.

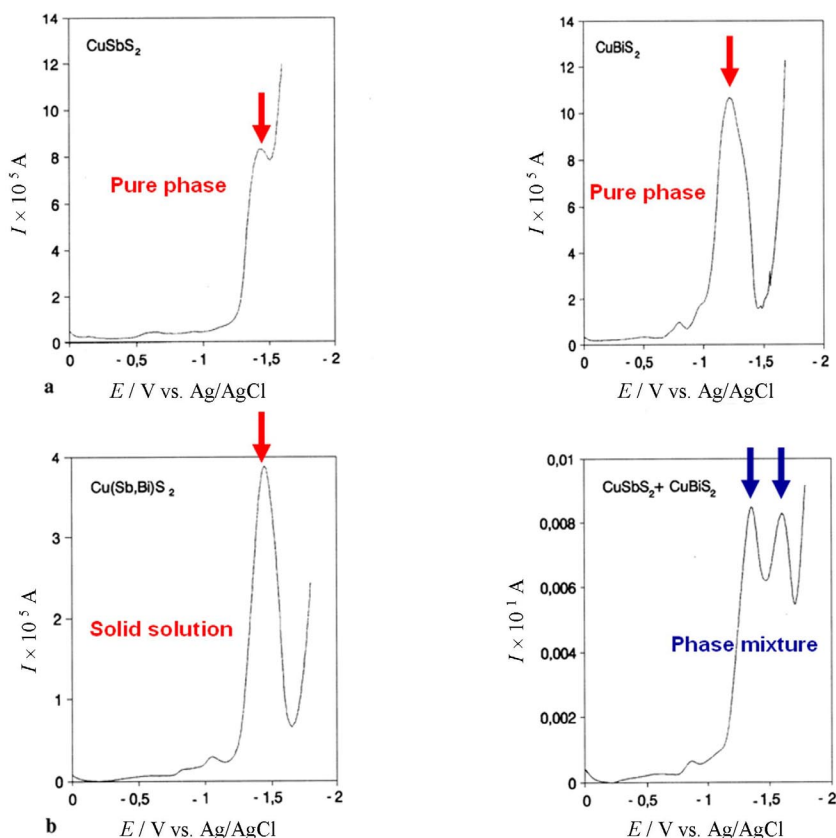**Fig. 7** Differential pulse voltammograms of reduction of (a) the pure phases $CuSbS_2$ and $CuBiS_2$, and (b) of the solid solution ($CuSbS_2 \cdot CuBiS_2$) and the powder mixture of $CuSbS_2$ and $CuBiS_2$. Adapted from ref. [152].

selected conditions, plots of $\log_{10}(i/A)$ on E are linear, providing Tafel slopes and ordinates at the origin characteristic of each pigment. Binary mixtures of such compounds also provided linear Tafel plots, the slopes and ordinates at the origin of which are intermediates between those of the individual pigments. Combination of all these Tafel parameters permits the mole fraction of each component in the binary mixture to be determined.

A very versatile approach to perform absolute determinations is the use of inner standards, namely, adding to the solid sample a standard of the selected analyte and a second electroactive solid component in fixed proportion. This last acts as an internal auxiliary standard. The "absolute" quantification of the mass, m_X, of component X and/or Y existing in a sample of mass m_S, can be obtained upon addition of a known mass, m_I, of an internal standard displaying an electrochemical signal separated from that of X and Y, whose magnitude A_I is proportional to m_I. Although the exact amount of X, Y, I species being effectively electroactive cannot be, in general, determined in SSEAC experiments, if well-homogenized mixtures are used and no inter-elemental effects appear, the magnitude of the electrochemical signals of X and Y relative to the inner standard will be proportional to the mass of such components relative to the mass of the standard; i.e., $A_X/A_I \propto m_X/m_I$. As far as the m_I/m_S ratio is known, one can also obtain the mass of the components X and Y relative to the mass of sample; i.e., $m_X/m_S \propto (A_X/A_I)(m_I/m_S)$. Notice that, in general, calibration using samples with known amounts of X and Y and the inner standard, is required.

In these circumstances, the methodology of standard addition method can be applied providing that: (i) the signal of the added analyte standard is identical to that of the analyte, (ii) the auxiliary inter-

nal standard yields an independent and well-defined voltammetric signal. Absolute quantification can then be obtained by means of VIMP [182]. A particular type of data analysis, the H-point standard additions method, can be used for the absolute quantification of two components displaying highly overlapping voltammetric signals [183,184]. An inner standard has been also used to quantify redox centres in complex hexacyanometalates [173].

4.4 Speciation and tracing

SSEAC techniques can be applied to identify the oxidation state of electroactive species able to be present in two or more oxidation states. This is the case of the study of Cu^{3+}–Cu^{2+}–Cu^+ transitions in the orthorhombic $YBa_2Cu_3O_{7-x}$ phase [185] and manganese complexes entrapped into zeolites [186]. The relative quantification of the species in two different oxidation states can be performed based on voltammetric data, under several favourable conditions, from the measurement of different electrochemical parameters [149,187]. This possibility is illustrated by the estimate of the Fe(III)/Fe(II) ratio in ceramic materials [149], and the identification/quantification of different lead and tin species [188] in archaeological glazed materials and speciation of manganese in carbonates and marine sediments [189,190] have been also reported.

Speciation involves also isomer discrimination, as is the case of *cis*- and *trans*-$Cr(CO)_2(dpe)_2$ and *trans*-$[Cr(CO)_2(dpe)_2]^+$ complexes (dpe = $Ph_2PCH_2CH_2PDh_2$) [191,192]. Another analytical possibility of SSEAC is the discrimination between different topological redox isomers; namely, molecules or ions placed in different locations in the solid structure. This is the case of different electroactive species attached to zeolites [143,144]. In several cases, different types of guest species can be associated to a given solid framework; in the case of Fe-ZSM5 zeolites, individual iron ions occupying reticular positions and voids in the aluminosilicate lattice are accompanied by iron oxide nanoclusters [145,146]. Apart from pigment identification in paintings [193], a case of speciation of particular interest in the archaeometric context is that of Maya Blue, an ancient nanostructured material, where SSEAC methods permitted the determination of the coexistence of both indigo and its oxidized form, dehydroindigo, attached to the palygorskite (a phyllosilicate clay) support, thus providing an economical explanation for the peculiar hue of the pigment and its variability [151]. These results permitted the definition of the Maya Blue pigment as a polyfunctional hybrid organic–inorganic nanostructured system precluding contemporary organic–inorganic hybrid materials [151,194]. Figure 8 compares the voltammetric responses of an indigo + palygorskite mixture and an archaeological sample from the Substructure IIC in the Yucatán site of Calakmul, possibly the most ancient sample of this pigment. The characteristic peaks of indigo, corresponding to the reduction and oxidation of this compound to leucoindigo and dehydroindigo, respectively, can be clearly seen in the voltammogram of the archaeological sample, in spite of large background current. Further, analysis of fine details of voltammetric data permitted the idea to be proposed that different types of preparation were used by the ancient Mayas [195] and that yellow and green pigments [196] and decorative plasters [197] using indigoid plus clay associations were prepared by this people.

Additionally, studies on the spatial distribution of electroactive centres in solid materials can be performed using SECM and related techniques [125–129]. "Local" analysis, performed on restricted regions of solid systems, can be made using the pencil electrode methodologies [95], of interest in the fields of archaeometry, conservation, and restoration [55]; in particular, this technique can be applied to the determination, layer-by-layer, of the composition of stratified corrosion layers in metals [198,199]. The variation of the time scale of voltammetric and chronoamperometric experiments can be applied to trace the variation of the concentration of electroactive species entrapped in the porous host deep in the particles [56,200,201]. This is based on the consideration that the progress of the electrochemical reaction through the solid involves charge transfer across the same so that the electrochemical response at different times should be representative of the composition in the different regions of the particles.
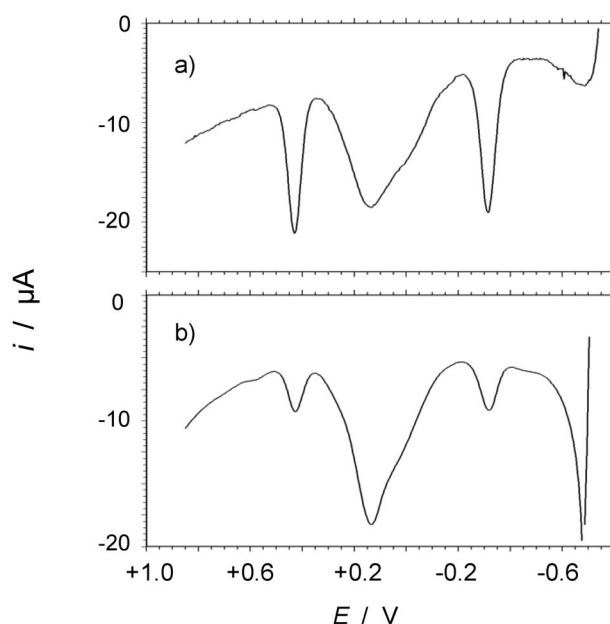
Fig. 8 Square-wave voltammogram of: (a) indigo (1 % w:w) + palygorskite mixture, (b) Maya Blue sample from the Substructure II-C in the archaeological site of Calakmul in contact with aqueous 0.485 mol kg^{-1} sodium acetate buffered solution, pH 4.85, Ag/AgCl (3 mol dm^{-3} NaCl) reference electrode. The sample, dated in the Late Preclassical period, may be the most ancient sample of Maya Blue currently detected. Adapted from refs. [151] and [194] with permission.

4.5 Analytical strategies

Different analytical strategies can be used in order to obtain the desired information. Electrochemical methods for determining a given analyte can, in general, be affected by interfering species (whose analytical signal is superimposed or can directly distort the analyte signal) and matrix effects (species disturbing the signal from the analyte by complexation, adsorption, etc.). The strategies include, apart from the variation in electrochemical conditions (technique, parameters such as potential scan rate in cyclic voltammetry or frequency in square-wave voltammetry, etc.) the sequential use of different electrolytes [202] or the application of constant polarization steps prior to electrochemical runs [203]. The combination of these strategies permits the definition of analytical sequences to identify different components between closely related families [204]. Other strategies can involve the use of magnetic fields to induce DNA hybridization [205].

Data treatment by means of bi- or multiparametric chemometric methods is also possible in SSEAC. These have been applied to voltammetric data in order to discriminate between different species displaying more or less similar electrochemical responses. Peak potentials and peak currents from cyclic, differential pulse, and square-wave voltammetries are typically used for the purpose of identification, but other parameters characterizing the shape of the voltammetric curves (peak width, peak to half peak separation, onset potentials), including Tafel slopes and ordinates at the origin can be used [206,207], and peak current and/or peak area ratios [149,208]. Principal component [209] and cluster analysis [149,195] multivariate chemometric methods have been applied to SSEAC.

Additionally, an electrocatalytic effect exerted by the solid materials on selected electrochemical processes can be utilized to obtain information on the composition of solids [166–169,210–212], including organic and pharmaceutically active compounds [213–217]. Here, the electrochemical oxidation/reduction process of an auxiliary species in solution phase is catalytically enhanced at sample-mod-

ified electrodes relative to that occurring at unmodified electrode. In several instances, the electrochemical information can be used to obtain wider analytical information; reported applications include monitoring solid state reaction kinetics [218,219], tracing temperature profiles in fired monuments [181,208], authentication of archaeological pieces [220], and dating archaeological materials [221–224]. As recently reviewed [225], studies include applications to environmental analysis [226,227] and pharmacology, including estimation of anti-oxidative properties of vegetables [228,229]. A number of electroanalytical applications to determine analytes in solution based on electrocatalytic processes occurring carbon paste electrodes incorporating a wide variety of modifiers are known and are available in recent reviews [104–107,230].

5. CONCLUSIONS

SSEAC has been established as a consolidated research field with a constantly increasing number of publications of developments and applications. The SSEAC methods are characterized by their versatility, high sensitivity, and accessibility because of the ordinary electrochemical instrumentation that is needed. A variety of analytical information on the structure and chemical and mineralogical composition of solids, even of complex systems, can be obtained from the electrochemical data. Compositional information, both qualitative and quantitative, can be achieved by voltammetry and coulometry. Speciation of components in solid materials relative to their oxidation state and/or coordination environment and even tracing of space distribution of electroactive species are also available.

Future research in this field could be oriented in two main directions: to develop theoretical approaches in order to complete the modelling of the involved electrochemical processes, and to increase the scope of applications of SSEAC by means of the use of new materials as electrodes, the exploitation of the capabilities of nanoelectrochemical techniques, and hyphenation with other non-electrochemical methods.

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