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Review

Applications of electrochemical techniques in mineral analysis

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ABSTRACT

This review, covering reports published in recent decade from 2004 to 2013, shows how electrochemical (EC) techniques such as voltammetry, electrochemical impedance spectroscopy, potentiometry, coulometry, etc., have made significant contributions in the analysis of minerals such as clay, sulfide, oxide, and oxysalt. It was discussed based on the classifications of both the types of the used EC techniques and kinds of the analyzed minerals. Furthermore, minerals as electrode modification materials for EC analysis have also been summarized. Accordingly, research vacancies and future development trends in these areas are discussed.

Contents

1. Introduction

Mineral analysis, an important branch of mineralogy, is to provide quantitative or qualitative methods to predict and monitor the mineral structure, formation or composition [1]. With this purpose, accurate mineralogical characterization or chemical identification of the minerals has to be carried out using light microscopy, X-ray fluorescence (XRF), X-ray diffraction (XRD), electrochemical (EC) techniques, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX), etc. [1]. Therein, EC instrumentation could offer powerful contributions to

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Abbreviations: AFM, atomic force microscopy; ASV, anodic stripping voltammetry; CPE-mineral, carbon paste electrode-mineral; CV, cyclic voltammetry; EAC, electron-accepting; EC, electrochemical; EDC, electron-donating; EIS, electrochemical impedance spectroscopy; LSV, linear sweep voltammetry; MMT, Montmorillonite; PBER, packed-bed electrochemical reactor; SEM/EDX, scanning electron microscopy with energy dispersive X-ray spectroscopy; SWa-1, Ferruginous smectite; SWV, square wave voltammetry; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction; XRF, X-ray fluorescence.

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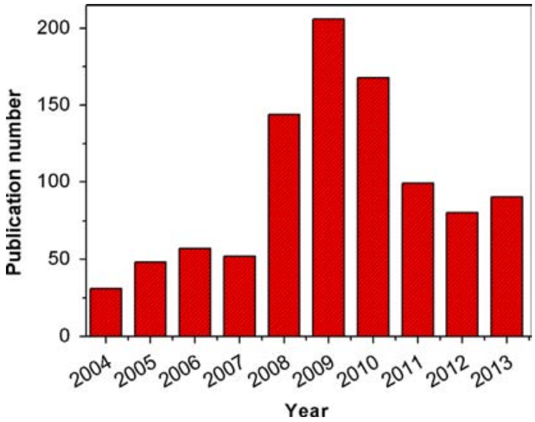

Fig. 1. Number of publications of mineral-related EC analysis from 2004 to 2013. (Source: Scopus).

Table 1
Summary of EC techniques applied for analysis of different minerals.

EC techniques used	Analytes and mineral Matrix	Ref.
CV	Catechol, soil	[2]
CV	Sulfide mineral	[8]
CV	Sulfide copper minerals	[14]
CV	Galena, sulfide mineral	[15]
CV	Platinum-carrying minerals	[18]
CV	Clay minerals	[24–26]
CV and potentiometry	Arsenopyrite mineral	[6]
CV and chronopotentiometry	Iron oxide minerals	[13]
CV and EIS	Sulfide minerals	[19]
CV, EIS and rest potential measurements	Pyrrhotite (Fe$_{(1-x)}$S)	[20]
SWV	South African chromite ore	[1]
SWV	Minerals and ceramic materials	[17]
Abrasive stripping voltammetry	Sulfide minerals	[21]
Square wave anodic stripping voltammetry	Cadmium, soil	[22]
LSV and chronoamperometry	Sulfide minerals	[23]
Potentiometry	Sulfide mineral	[29]
EIS	Oxysalt minerals	[28]
Electrolysis and fuel cells	Magnesium silicate rock	[12]

investigation of mineral treatment processes such as catalysis, polycondensation, deposition and flotation [2–5]. EC process can directly convert a chemical event taking place in a solution at the electrode/electrolyte interface to a measurable electronic signal such as current (*amperometric*), potential or charge accumulation (*potentiometric*), and altered conductive properties (*conductometric*). It was with the advantages of simple and portable instrumentation, low cost, rapid response, high sensitivity, etc. [2,6,7]. Major focus of this review herein is on the commonly used techniques such as voltammetry, potentiometry and electrochemical impedance spectroscopy (EIS). Some other representative references are also selected to cover the EC-related mineral analysis as comprehensive as possible. In addition, because some of the minerals possess certain properties such as stable, inexpensive as well as cation exchange capacity, film formation ability and catalytic properties, they could be used as excellent assisting reagents to make the electrodes or EC sensors more stable, selective, and accurate, etc. [8–10] for themselves analysis or other analytes detection or interaction investigations. For example, Zen and Kumar reviewed that the clay mineral can be used for chemically modified electrodes to provide a suite of sensor options [11].

As can be seen in Fig. 1, research on mineral-related EC analysis has attracted much attention in recent decade (from 2004 to 2013), especially since 2008. It clearly indicates that many scientists are participating into this research field. However, as far as we know, scarce review has been reported to summarize the applications of EC in mineral analysis and mineral as electrode (or modification) materials for EC method development.

Herein, combining with the latest decade research articles, both aspects about EC techniques used in mineral analysis and mineral used as electrode (or modification) materials for sensitive and selective analysis from 2004 to 2013 are reviewed. Consequently, their research vacancies as well as the development potential and prospects of these fields are discussed.

2. Applications of EC techniques for mineral analysis

2.1. Types of the EC techniques used in mineral analysis

Based on the EC definition, electrolysis, fuel cells [12] and voltammetric methods, chronopotentiometry, EIS [13], etc., all belonged to EC techniques. As can be seen in the summarization of Table 1, the most commonly used EC techniques in mineral analysis were voltammetric methods [1,2,6,13–18] such as cyclic voltammetry (CV) [2,13,14,16], square wave voltammetry (SWV) [1], linear sweep voltammetry (LSV) [17] as well as potentiometry and EIS [19,20], etc. The EC methods can be used in different purposes of mineral-related analysis, taking the studied voltammetric methods as representatives (see Table 2), such as in composition and impurity analysis [1], trace metal detection [21,22], EC behaviors in process of leaching [8,14] and flotation [19], kinetics [15] and catalytic [2] study, stability [23], redox [24–26] and surface [20] properties, etc., of different minerals.

For example, in a method to quantitatively determine boron in minerals and ceramic materials, SWV was used to record for those modified electrodes immersed into 0.10 M NaCl with 0.25 M mannitol and provided well-defined stripping peaks at -0.85 and -0.15 V vs. Ag/AgCl for the oxidation of Zn and B, respectively. Results for boron-containing minerals and ceramic frits were in excellent agreement with those obtained by a potentiometric reference method [17]. Jung et al. assessed the application of anodic stripping voltammetry (ASV) for *in situ* determinations of both total concentration and speciation of dissolved heavy metals (Cd, Cu, Pb and Zn) in acid mine drainage. It was obtained that ASV after wet oxidation was sensitive enough to determine the total concentration of dissolved Cd, while not so effective for determining total Cu. For dissolved Pb, the concentrations determined by ASV after wet oxidation were generally consistent with those by inductively coupled plasma atomic emission spectrometer. The determination of total dissolved Zn by ASV after wet oxidation appeared to be unsatisfactory for the samples with high Cu content, possibly because of the interference resulting from the formation of Zn–Cu intermetallic compounds on the mercury coated electrode [27]. Abrasive stripping voltammetry was also tested in the direct measurement of trace metals in anoxic, sulfidic marine sediments from a small and shallow (0.2–1 m) marine lagoon. Trace amounts of sample compounds are transferred to the graphite electrode surface and EC reduction or oxidation processes were followed by the CV in 0.55 M NaCl or seawater as an electrolyte (see Fig. 2). After the preelectrolysis at potentials ranging from -1.0 to -1.5 V (vs. SCE), a well-defined anodic stripping peak corresponding to the oxidation of metal deposits appeared at around -0.74 V (vs. SCE). The results confirmed that voltammetry was a well alternative tool for trace metal detection in peloid marine sediments [21].

In addition, EIS could also be used as a measure of surface coverage by the mineral scale. Results showed that the mass of mineral deposits accumulated on the metal surface was well correlated with the constant-phase element capacitance. The constant-phase element capacitance was sensitive enough to as small as <0.1 mg changes in the mineral mass deposited on the electrode. Unlike traditional methods for measurement of mineral deposition, the EIS allowed *in situ* semicontinuous measurements of overall mineral deposition, and its sensitivity provided efficient means for early detection of mineral deposition [28]. Besides the EC reaction in solution phase, the development of a graphite paste electrode made it possible to investigate powdered sulfide mineral samples, which ensured that the measurement conditions were as close as possible to the real leaching conditions. The graphite paste electrode made it possible to conduct EC measurements reproducibly and reliably [21,29].

2.2. Kinds of analyzed minerals

2.2.1. Clay minerals

Clay minerals often contain redox-active structural iron that participates in electron transfer reactions with environmental pollutants, bacteria, biological nutrients, etc. Using EC approaches for measuring the redox properties of structural Fe in clay minerals makes great sense but has proven to be difficult because the lack of reactivity between clay minerals and electrodes. To overcome this limitation, Gorski et al. [24–26] did a lot of valuable work. In an EC cell, one electron-transfer mediating compound was used to facilitate electron transfer between structural Fe in clay minerals and a vitreous carbon working electrode. Using this approach, the electron-accepting (EAC) and -donating (EDC) capacities (Q_{EAC} and Q_{EDC}) were quantified at applied potentials (E_H) of -0.60 V and $+0.61$ V (vs. SHE representing standard hydrogen electrode), respectively, for four natural Fe-bearing smectites (Ferruginous smectite (SWa-1), Na-rich montmorillonite (MMT), and two nontronites). The Q_{EAC} and Q_{EDC} values could be used as benchmarks in future studies examining the extent of reduction and oxidation of Fe-bearing smectites [24]. Subsequently, as can be seen in Fig. 3, an approach was further developed to directly assess the redox properties of a natural Fe-bearing smectite (SWa-1, 12.6 wt% Fe) with mediated EC reduction and oxidation. It was obtained that the Fe^{2+}/Fe^{3+} couple in SWa-1 was redox-active over a large range of potentials (from $E_H = -0.63$ V to $+0.61$ V vs. SHE). Spectroscopic analyses were also applied to assist the EC experiments. The final results were indicative of the importance of Fe-bearing clay minerals as redox-active phases in a wide range of redox regimes [25]. MMT/polyaniline nanocomposites could be obtained by intercalation of aniline monomer into the clay MMT modified with different cations (Na^+, Cu^{2+}, Fe^{2+}) by cation exchange and subsequent oxidative polymerization of the aniline in the clay interlayers. CV methods were used to study the

Table 2
Summary of different purposes of mineral analysis by EC techniques.

Purpose and analytes	EC techniques used	Ref.
Composition and impurity analysis	SWV	[1]
Measurement of trace metals in anoxic, sulfidic marine sediments	Abrasive stripping voltammetry	[21]
Trace cadmium detection	Square wave anodic stripping voltammetry	[22]
Bioleaching of chalcopyrite and bornite	CV	[8]
The EC behavior of sulfide copper minerals in leaching process	CV	[14]
EC performance of pentlandite in collectorless flotation	CV and EIS	[19]
EC kinetics of galena	CV	[15]
Catalytic study	CV	[2]
Stability of sulfide minerals	LSV and chronoamperometry	[23]
Redox properties of structural Fe in clay minerals	CV	[24–26]
Surface properties of pyrrhotite	CV, EIS and rest potential measurements	[20]

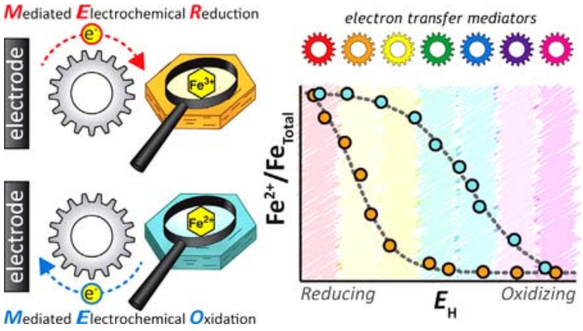

Fig. 3. Graphical abstract figure of Ref. [25] for studying the redox properties of structural Fe in clay minerals by using a suite of one-electron-transfer mediating compounds to facilitate electron transfer between structural Fe in clay mineral and a working electrode. (Copyright 2012, American Chemical Society).

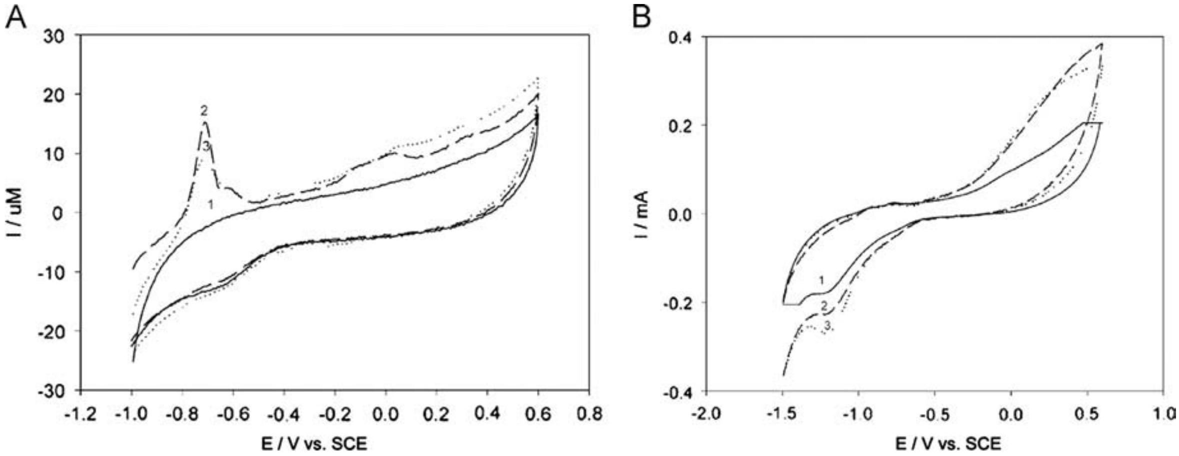

Fig. 2. (A) CVs of abrasively transferred peloid sediment microparticles in 0.55 M NaCl/HCl, pH 2–3; accumulation time: (1) 0, (2) 60, (3) 120 s at $E_{acc} = 1.0$ V; scan rate = 100 mV/s. (B) CVs of peloid sediment suspension in the seawater at the paraffin-impregnated graphite rod. Anodic going scan after accumulation of: (1) 0, (2) 60, (3) 120 s at $E_{acc} = 1.5$ V; scan rate = 100 mV/s [21]. (Copyright 2007, Wiley-VCH).

electrochemical behavior of the polymers extracted from the nanocomposites and a good EC response was obtained [30,31]. Epoxy coatings containing polyaniline/organophilic MMT powders were prepared on the surface of AZ91D magnesium alloy. EIS data showed that that the polyaniline/organophilic MMT coating retained its high corrosion protection for AZ91D magnesium alloy after 6000 h of immersion [32].

An electrical triple-layer model was proposed to describe the EC properties of clay minerals. This model included a speciation model of the active crystallographic surface sites as well as a classical description of the Stern and diffuse layers. The model showed good agreement with the experimental data for reasonably choosing parameters close to the priori values determined from quartz and gibbsite [33]. Moreover, Maya Blue-type specimens can be prepared from indigo (1 wt%) attached to kaolinite, MMT, sepiolite, silicalite, and palygorskite, EC methods such as SWV, EIS, etc., confirmed the presence of a significant amount of dehydroindigo and isatin accompanying indigo and other minority organic compounds in all solid samples. The EC data also permitted the estimation of the indigo loading in archeological Maya Blue to be 0.2–1.5 wt% [34]. In addition, the trace cadmium in soil can be successfully detected using Nafion/stannum film-modified molecular wire carbon paste electrodes by square wave anodic stripping voltammetry [22].

2.2.2. *Sulfide minerals*

The sulfide minerals, which containing sulfide (S^{2-}) as the major anion, are economically important as metal ores. They are the mostly studied class of minerals related to EC techniques herein. Sulfide mineral dissolution in aqueous media occurs with different mechanisms. Most important factor in the anodic dissolution of mineral sulfides is the formation of a reaction product layer, which affects the mass transfer rate, often the rate determining step of the overall reaction. Thus, potentiostatic measurement method for leaching behavior of sulfide minerals has been developed to evaluate the factors affecting sulfide mineral dissolution [29]. The transfer mode of reacting charge on surface of the ore particles in the system of sulfide minerals flotation separation has also been analyzed. The results demonstrated that when the EC reaction took place on the surface of sulfide ore, the transfer of reacting charge was related to mineral property, mineral surface character, property of pulp fluid phase and manner of pulp potential contro1. This work showed significance in the potential control of sulfide ore flotation and the flotation separation of complex sulfide ore [35].

Precious metals, gold in particular, are naturally contained in a wide range of sulfide mineral systems [36]. Since the discovery of gold dissolution in cyanide solutions by Carl Wilhelm Scheele [37], numerous studies have been carried out to elucidate the mechanisms and dominating factors during this reaction [38]. Because sulfide minerals could dissolve in aerated cyanide solutions making gold cyanidation a process difficult to optimize, a number of investigations were performed to understand how the resulting dissolution products would interfere with gold leaching [36,38]. Because most of the sulfide minerals are endowed with significant electric conductivity allowing charge transfer at their surface of gold–sulfide contacts, EC techniques were shown to be an effective tool to know the influences of certain sulfide minerals on gold cyanidation. Azizi and Larachi's group did a series of systematically valuable works on this subject [36,38–40]. Firstly, a detailed study to assess the importance of passivation phenomena and galvanic interactions during gold cyanidation was performed. Mineral disc electrodes consisting of a sulfide-rich industrial ore and major sulfide components were set up along with an Au/Ag electrode for gold leaching rate tests. Cyanidation experiments were conducted by integrating the Au/Ag electrode with one of the two mineral electrodes in one or two EC cells. It was found that gold dissolution rate was controlled by positive galvanic interactions rather than by passivation in one EC cell, while gold leaching was controlled only by positive galvanic effects giving rise to high galvanic currents when gold and mineral electrodes were immersed in two separate cells. Moreover, all minerals had a negative effect on the leaching rate of gold and the mineralogy of the ore influenced its dissolution [38]. Because permanent galvanic contacts between slurried sulfide-rich ores and gold rotating disc electrodes are a little difficult to reach, corrective trend of galvanic interactions inherently presenting within the ore grains would be influenced. Thus, a new packed-bed electrochemical reactor (PBER) was developed and tested to decouple and quantify the individual contributions of galvanic interactions and passivation phenomena on gold leaching rates during the cyanidation of sulfide-rich mineral [36]. Moreover, leveraging strategies to increase gold cyanidation in the presence of sulfide minerals-PBER approach was further investigated [39]. Furthermore, a multi-layer PBER approach was established and applied for studying the leaching behavior of associated and free (silica-trapped) gold from a series of synthetic multi-mineral systems consisting of pyrite, silica, Au, and subsequently chalcopyrite, sphalerite or chalcocite. Using the new PBER configuration during cyanidation, it was able to distinguish the effect of gold distribution and mineral galvanic associations on both Au recovery and reactivity of sulfide-rich ores as well as to investigate the effects of varying the cathode-to-anode area ratio on gold leaching from multi-mineral systems [40].

Besides the precious metals, others such as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), covellite (CuS), pyrite (FeS), pentlandite (FeS_2), galena (PbS) and Cu–Zn sulfides, are also sulfide minerals being studied by EC techniques [3,14–16,19,23,41,42]. The stability of pyrite, chalcopyrite, chalcocite, covellite, bornite and enargite at pH 2.0 in the absence and presence of thiocyanate has been investigated by LSV and chronoamperometry under conditions pertaining to the thiocyanate leaching of gold (pH 2.0 and 602–702 mV vs. SHE). The EC results indicated that the decomposition rate of all studied sulfide minerals increased with an increase in oxidation potential, thereinto, pyrite and chalcopyrite were the least reactive while chalcocite and bornite were the most reactive sulfides. The oxidation rate of enargite and covellite was higher than that of chalcopyrite and pyrite but much lower than that of bornite and chalcocite [23]. EC behaviors of pyrite and chalcopyrite were studied by measuring polarization curves and the EIS method in a NaCl solution under differential stress. The results from differential stress experiments indicated that there was a negative linear relation between potential difference and elastic stress [43]. Pyrrhotite ($Fe_{(1-x)}S$) samples from the Phoenix, Sudbury Copper Cliff North, Sudbury Gertrude West and Nkomati nickel mines were used for the EC measurements such as rest potential measurements, CV and EIS techniques. The EC results showed that non-magnetic pyrrhotite was the least reactive towards oxidation as well as the best collectorless flotation performance, while the magnetic pyrrhotite samples were much more reactive. Differences in EC reactivity were also observed for different magnetic pyrrhotite samples, which was indicative of the dependency of pyrrhotite reactivity on its provenance [20]. The EC behavior of sulfide copper minerals in leaching process was studied with suspending slurry of chalcopyrite, chalcocite and eovellite by a three-electrode system consisting of a Pt disk as a working electrode, saturated calomel as a reference electrode and Pt plate as a counter electrode. The results showed that Cu_2S was the easiest one to be oxidized while $CuFeS_2$ was the most difficult one in three minerals [14]. In addition, combined with X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), the EC techniques such as CV and chronoamperometry

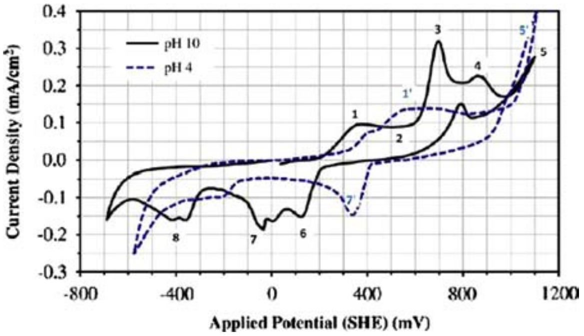

Fig. 4. Typical cyclic voltammograms for natural enargite at pH 10 (black, solid line) and pH 4 (blue, dashed line) obtained using a scan rate of 1 mV/s. The curves started at −420 mV, returned to the cathodic scan at 1000 mV, and terminated at −420 mV [44]. (Copyright 2013, American Chemical Society). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

were developed for characterization of the natural enargite (Cu_3AsS_4). As can be seen in Fig. 4, the effects of an applied oxidizing potential on the surface of natural enargite in pH 10 and pH 4 solutions were investigated and compared to a freshly polished natural enargite surface. Oxidative surface morphology of enargite and the formation of surface species were characterized and confirmed by AFM and XPS [44].

Flotation is a process in which valuable minerals are separated from worthless material or other valuable minerals. Since the floatability of sulfide minerals can be affected by the redox conditions on particle surface and in the pulp, it can be used as a parameter for the separation of sulfide minerals. The presence of reducing and oxidizing agents in the pulp was studied for pure samples of chalcopyrite and pyrite by Göktepe [3]. Pulp potentials were evaluated by manufactured mineral electrodes and with platinum electrode to counter the electrodes, as well as pH were also measured. A good correlation between pulp potential and recovery of chalcopyrite and pyrite was found when the potential was varied by the addition of H_2O_2 and NaSH as oxidizing and reducing agents, respectively [3]. The collectorless flotation includes self-induced flotation and sodium sulfide-induced flotation. Deng et al. studied the EC performance of pentlandite in both cases. Thereinto, CV, EIS and XRD analysis were applied. It was obtained that the pentlandite started to oxidize at 0 mV, and the hydrophobic product was elemental sulfur which reached the highest amount at ~300 mV. Addition of Na_2S was favorable for the self-flotation of pentlandite while the ferric ions that played an important role in the Na_2S-induced flotation were dissolved from the oxidation of mineral and oxidized the Na_2S to elemental sulfur [19]. EC technology was also introduced into studying the floatability of galena in some waste water samples from different processes of mineral processing plant in Fankou Lead–Zinc Mine. It was obtained that direct reuse of this waste water would result in disadvantageous influence on galena flotation [16].

2.2.3. Oxide minerals

Metal oxide minerals, e.g. iron oxide minerals, are electron acceptors. Thus using EC methods in a dual-chamber system of microorganism-iron oxide mineral, the redox properties of iron oxide minerals accomplishing the research of microorganism reduction in a new perspective was conducted. Therein, the iron oxide minerals acted as cathodes and were capable of accepting microbial electron. The results showed that microorganisms used iron oxide minerals as electron acceptors and hereby reduced them, and that iron oxide minerals could receive electron under the condition of 0.2 mA cathodic constant current [13]. EC techniques are also supplementary tools for studying oxide minerals. For example, the SWV analysis demonstrated that iron in the South African chromite ore was as Fe(II). Together with techniques of XRF, XRD, SEM, etc., a strategy for calculating the composition of each mineral could be developed [1].

2.2.4. Oxysalt minerals

This mineral class includes silicate, carbonate, sulfate and phosphate, etc. Especially silicon and oxygen constitute approximately 75% of the Earth's crust, which translates directly into the predominance of silicate minerals. An accurate and convenient approach for monitoring the rate of mineral deposition on metals in real time was developed. It involved use of an EC cell employing the metallic collecting surface as a working electrode. The working electrode served as both the surface for mineral deposition and a sensor for probing subtle changes resulting from the growth of mineral deposits at the metal–mineral–water interface. Moreover, the characteristics of different minerals evaluated in this study, i.e., calcium carbonate, calcium sulfate, and calcium phosphate, did not influence the constant-phase element capacitance measurement significantly [28]. In a thermodynamic efficiency analysis, exergy concept was used to assess CO_2 mineral sequestration process routes. Therein, EC steps (electrolysis and fuel cells) were used to produce aqueous HCl and NaOH reactant solutions. It was obtained that including electrolysis as one of the steps of a magnesium silicate mineral carbonation process route could result in input energy requirements. The requirements would exceed the output of a fossil fuel-fired power plant that produced the CO_2 bound to (hydro-) carbonates. Meanwhile, fuel cells were not efficient enough to change this [12]. EC splitting of calcium carbonate (e.g., as contained in limestone or other minerals) was explored to form dissolvable hydroxides for absorbing, neutralizing, and storing CO_2, and for restoring, preserving, or enhancing ocean calcification [45]. A method for quantitatively determining boron in minerals and ceramic materials was established based on the abrasive attachment of ZnO mixtures plus sample to paraffin-impregnated graphite electrodes. The quotients between the peak areas and the peak currents for the stripping oxidation of B and Zn varied linearly with the molar ratio of B and Zn in the mixture, thus providing the EC method for determining the boron content in solid samples [17].

2.2.5. Other minerals

Based on a CV method, carbon paste electrode was employed for arsenopyrite mineral characterization in non-aqueous solution. Arsenopyrite yielded well-defined cyclic voltammetric responses with well-defined oxidation (from −0.7 to 0.7 V vs. Ag/AgCl) and reduction (from −1.0 to 0.8 V vs. Ag/AgCl) peaks [6]. Pt–Te_2 and Pt–Bi–Te are two important platinum-carrying minerals usually found in altered platinum reserves. Fundamental interactions of potassium ethyl xanthate with these minerals were studied by electrochemically controlled contact angle measurements and voltammetry. The EC investigations revealed that Pt–Te_2 was more noble than Pt–Bi–Te at potentials lower than 300 mV (vs. SHE) in sodium tetraborate buffer solution. Both the minerals showed increased anodic currents when polarized at 0.3 V (vs. SHE) in a 0.05 M $Na_2B_4O_7$ solution containing 1.0 mM potassium ethyl xanthate. According to the results of the rest potential measurements, the formation of dixanthogen was thermodynamically favorable and the very high rest potentials were attributed to the catalytic effect of platinum on the oxygen reduction reaction [18].

3. Minerals as electrode (modification) materials for EC analysis

The minerals can not only be analyzed by the EC methods but also could affect the analysis results of the EC simultaneously or assist to establish the EC methods for analysis of the minerals themselves or other analytes or for interaction investigations. For example, natural chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) could be used as working electrodes [46–49]. The electrode surfaces were studied by EC techniques such as CV, EIS, chronoamperometry, potentiostatic and potentiodynamic polarization [46,49]. XRD and X-ray photoelectron spectroscopy (XPS) were used to analyze the minerals and product layers on the surface before and after the electrodissolution. XPS results showed that a metal-deficient sulfide film ($Cu_{1-x}Fe_{1-y}S_{2-z}$) consisting of cuprous sulfide (Cu–S) and iron sulfide (Fe–S) bonds was the most plausible copper and iron containing sulfide phase which passivated the surface of chalcopyrite [49]. At advanced oxidation states, the formation of Fe(III) species containing oxygen was detected for both electrodes and Cu(II) species containing oxygen were additionally detected for chalcopyrite. At high oxidation states, both minerals showed a pseudoinductive loop in the equivalent circuit, which resulted from the active electrodissolution of the minerals taking place through a surface film previously formed [46]. Using pyrite crystal as the working electrode, the electrochemistry of dithiophosphinate adsorption on pyrite was investigated by CV and diffuse reflectance infrared Fourier transformation spectroscopy at oxidizing potentials under acid, neutral, and alkaline conditions. CV study showed that the mineral surface was covered by porous ferric oxyhydroxide species [50]. Knowledge of bacterial role during chalcopyrite oxidation was with great importance to improve the efficiency of bioleaching performance. Thus the oxidative dissolution of a massive chalcopyrite electrode by *Acidithiobacillus ferrooxidans* was estimated by EIS and AFM. Thereinto, a massive chalcopyrite as a working electrode was applied in a Tait-type EC cell in acid medium for different immersion times in the absence or presence of bacterium. The differences obtained in the EIS diagrams were correlated with the adhesion process of bacteria on the mineral surface [47]. Besides the utilization of massive samples of the mineral, chalcopiryte microparticles could also be used as working electrodes. Thus the microelectrochemistry of chalcopyrite was studied in sulfuric acid solutions, focusing the study on its behavior at transpassive potentials. It was found that microparticles with sizes typically found in chalcopyrite concentrates (20–100 μm) could be leached to completion in less than 4 min under the potential of 1.2 V (vs. SCE) [48].

Using galena as a working electrode, voltamperograms of the EC analysis in alkaline xanthate-bearing solutions have shown that the lead xanthate and galena oxidation products (i.e. lead sulfate, lead thiosulfate and lead hydroxide) were formed on the surface of the polarizable galena electrode in the xanthate-bearing solutions with varied concentrations and pH values [15]. Manganese dioxide with 3×3 tunnels bearing the crystallographic structure of the mineral todorokite could be used as a new cathode material for zinc ion cells, simultaneously, its structural and EC properties could be investigated. Compared to the conventional medium-sized 2×2 tunnels of cryptomelane, the large 3×3 tunnel of todorokite was favorable for fast Zn^{2+} diffusion to the inner region of a particle. In the EC studies, a discharge capacity of 108 mA h/g at C/2 and a good rate performance was observed in the potential range from 0.7 V to 2.0 V [51].

Carbon paste electroactive electrodes as a working electrode could be made by mixing minerals (chalcopyrite or bornite or mixture of chalcopyrite and bornite), graphite and solid paraffin (named CPE-mineral electrode) [8,41,52,53]. Then using graphite rod as a counter electrode and Ag/AgCl (3.0 M KCl) electrode as a reference electrode, a three-electrode system could be constructed. Results of CV tests showed that the oxidation and reduction mechanisms of bornite and chalcopyrite were similar. Although the addition of bornite or chalcopyrite could increase the current density during oxidation process at 300–700 mV, it did not change the oxidative and reductive mechanisms. The EC results confirmed the bioleaching study results in the work [8]. In addition, the applicability of CPE-mineral electrode was tested to study the dissolution mechanisms of minerals in powder form and in flotation concentrates [41,52]. A potentiodynamic strategy to find the dissolution mechanism of galena was presented [41]. The dissolution mechanism of chalcopyrite was studied on carbon paste electrodes with chalcopyrite (CPE–chalcopyrite) in 1.7 M sulfuric acid. A sequence of anodic potential pulses and CV were applied to characterize the EC behavior of the CPE–chalcopyrite electrode. Characterization of the electrode surface state of each electrochemically modified CPE–chalcopyrite and the amount of dissolved copper exhibited five potential regions where the chalcopyrite dissolution mechanism changed [52]. A CPE–zinc concentrate electrode was prepared for studying the anodic dissolution in 1.7 M sulfuric acid of the zinc concentrate (63.4% sphalerite, 20.1% pyrite, 5% chalcopyrite, 0.33% galena, 0.45% tetrahedrite ($Cu_{12}Sb_4S_{13}$), and 0.4% arsenopyrite (FeAsS) derived from the flotation process. The surface of the electrode was characterized by CV and the resulting solutions were analyzed by ASV. The obtained results showed that progressive anodic dissolution of zinc concentrate in the whole potential range ($0 \le E_{appl} \le 600$ mV) was significant. Moreover, the obtained results demonstrated an alternative for hydrometallurgical processing of complex zinc concentrates [54]. The EC behaviors of a CPE–marmatite electrode with the chemical leaching of Fe^{3+} ions, or the microbial leaching using *Acidithiobacillus ferrooxidans*, were compared. The CV results of the electrode in the presence and absence of bacterial strains indicated that the leaching process of marmatite was carried out by the different reactions occurring in the interface of the marmatite electrode-leach liquid. And the microbial leaching of marmatite could be accelerated by the applied potential [53].

Due to the conductive character of clay layer, high stability, good biocompatibility as well as the cation exchange capacity, film formation ability and catalytic properties (see Fig. 5A), clay mineral can be used to modify the electrodes for electroanalysis, photocatalysis and biosensors [10,11,55–57]. Catechol is a precursor of organic matter in soils and can be catalyzed and polycondensed by clay minerals to produce humic acid. Thus the catalysis and polycondensation of catechol and glycine by clay minerals was carried out using screen-printed carbon electrodes coupled with CV, which was confirmed to be a rapid and convenient method. The order of catalytic ability was finally shown to be ferruginous smectite > kaolinite > Na–MMT. Furthermore, porosity of clay film was found to possibly affect the clay-modified electrodes in studying catalysis and polycondensation of catechol

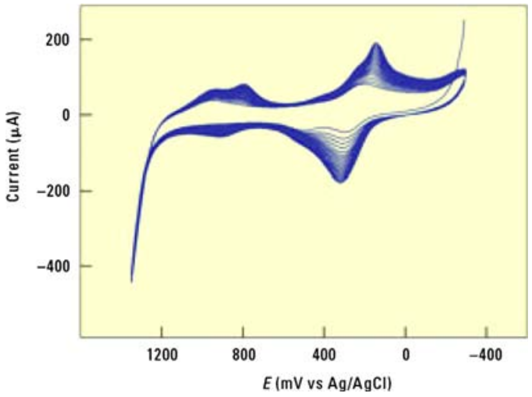

Fig. 5. Typical continuous response for 20 cycles of voltammetry of a nontronite-modified carbon paste electrode with 2 mM $Fe(CN)_6^{3-}$ in 0.1 M pH 2 KCl/HCl at a scan rate of 50 mV/s [11]. (Copyright 2004, American Chemical Society).

[2]. Nontronite belongs to one iron-rich clay, it can be converted into an efficient catalyst by EC formation of hybrid Prussian blue $[Fe^{3+}Fe(CN)_6]$ and ruthenium purple $[Fe^{3+}Ru(CN)_6]$ directly inside the matrix. As can be seen in Fig. 5, in the typical hybrid Prussian blue preparation, the nontronite modified carbon paste electrode was electrochemically treated with $Fe(CN)_6{}^{3-}$ in pH 1–3 KCl/HCl solution for several continuous cycles. The larger quantity of Fe^{3+} in the interlaminar structure of nontronite can effectively assist the hybrid Prussian blue formation [11]. Derivatives of clay minerals can be used for the selective detection, using their size as a differentiating factor. For example, functionalized nanohybrid materials based on kaolinite were obtained by grafting different sizes of ionic liquids in the interlayer spaces of kaolinite. Using glassy carbon electrodes coated with a thin film of the modified kaolinite, voltamperometric detection of some anions with different sizes (thiocyanate, sulfite and ferricyanide ions) was achieved [58]. MMT belongs to one very rich clay mineral and consists of layers of two tetrahedral silica sheets sandwiching one octahedral alumina sheet. Then an expanded graphite electrode modified with intercalated MMT was constructed for the EC determination of catechol. Intercalated MMT could significantly improve the peak current of catechol on the cyclic voltammograms due to the remarkably increased specific surface area of MMT after intercalation. A detection limit of 1.13 μM (S/N=3) for catechol was obtained based on the amperometric sensor [59]. Na–MMT could be utilized for the immobilization of thionine, horseradish peroxidase and the secondary anti-zeranol antibody to establish an immunosensor to detect zeranol. The proposed immunosensor showed good reproducibility, selectivity and stability. A low detection limit of 3 pg/mL was obtained for zeranol [60]. In addition, resonance Raman, FTIR, XRD, UV–vis–NIR, electron paramagnetic resonance, X-ray absorption at Si K-edge and electron microscopy were employed for characterizing the products formed through EC oxidation of intercalated anilinium ions inside the cationic MMT clay. It indicated that the layer silicate structure was not affected by the anilinium oxidation between the layers [61]. Moreover, the MMT can be modified with histidine to enhance its immobilization capability for the biomolecules. After a successful immobilization of Laccase enzyme with the histidine–MMT matrix on a glassy carbon electrode, application in catechol biosensing was achieved [56]. For MMT-calcium clay, it has strong adsorptive ability, high chemical and mechanical stability properties. So a MMT–Ca modified CPE was developed for the sensitive determination of methocarbamol using the square-wave adsorptive anodic stripping voltammetric method. Detection limits of 3×10^{-9} and 1.2×10^{-8} M methocarbamol were achieved in the bulk form and in spiked human serum, respectively [62]. EC character of copper-plated screen-printed carbon electrodes can be modified by different clay minerals. The oxidation of copper could be promoted by three clay minerals modified on copper-plated electrodes. Electrocatalysis of dopamine can be observed in the ferruginous smectite modified copper-plated electrode with a linear range of 0.5–10 μM (R=0.9997) by flow injection analysis [10]. Single-molecule fluorescence spectroelectrochemistry of cresyl violet adsorbed on the clay-modified surface was observed. Due to redox reaction controlled by CV, the fluorescence intensity of single molecules exhibits on/off switching [63].

Arsenopyrite mineral could be used as a new indicator electrode for the potentiometric titrations of acids and bases in acetonitrile and propionitrile. KOH, $HClO_4$ and tetrabutylammonium hydroxide proved to be very suitable titrating agents for these titrations [6,64]. Natural monocrystalline pyrite [65–67] and chalcopyrite [66,67] could also be used as new indicator electrodes for the potentiometric titration of weak acids in acetonitrile, propionitrile, benzonitrile [65], *tert*-butanol and *iso*-propanol [66] and they were studied. The investigated electrode showed a linear dynamic response for *p*-toluenesulfonic acid concentrations in the range from 0.1 to 0.001 M, with a Nernstian slope of 74 mV [65] or 48 mV [66] per decade. The response time was less than 11 s and the lifetime of the electrode was long. The advantages of the electrodes were long-term stability, rapid response, reproducibility, easy preparation and low cost [65,66].

In addition, using the clay mineral MMT as both stabilizer and carrier, silver nanoparticles could be successfully synthesized via a rapid and convenient EC method scheme, which was composed of a two-electrode setup containing 15 mL of MMT-contained electrolyte solutions [68]. To enhance silver effectiveness for oxygen reduction reaction, pillared clay was used as a support for silver nanodispersion. Then the Ag-pillared clay composite homogenized with 10 wt% of nanodispersed carbon black can be applied on a flat glassy carbon surface and used as an electrode material for investigating oxygen reduction reaction in an O_2-saturated aqueous 0.1 M NaOH solution [69]. A novel technology could be constructed combining EC process catalyzed by manganese mineral with electro-assisted coagulation process. It was found that the manganese mineral could catalyze the EC process dramatically. A proposed mechanism of manganese-mineral-catalyzed electro oxidation–reduction process was also discussed in the publication [9]. Using everyday mineral water as an electrolyte, a new EC micromachining method could be established. The advantages of the new method included totally green machining, high precision, high efficiency, and low-cost [70].

4. Conclusions and future trends

As an analytical method, EC techniques have been widely penetrated into various scientific areas of mineral-related analysis. In addition, mineral could be used as electrode (modification) materials or an indicator to assist in efficient development of EC techniques. EC has been proved to be a rapid, convenient and low-cost analytical method in this area. However, as summarized, fewer publications have been reported than those expected until now. It should be not because application in little scale, but should be due to no fresh scope was exploited. It has been attracting increasing attention in recent years, especially recent 2 years. Accompanying with new methods to pre-processing the solid minerals into solution phase, EC assays will be more appropriately used in analyzing and concentrating valuable minerals. Moreover, development of some new electrodes such as carbon paste electrode and screen-printed electrode will provide good compatibility between the solid mineral and the EC methods. This will make great sense in solid-state electrochemistry for natural mineral analysis. In addition, new methods should be developed for mineral modification on the electrode surface, which will enhance the performance of the EC sensors in analytical fields. With further investigation of EC and the minerals, they will provide better scientific platforms for each other. Subsequently, much more great achievements will be made in these areas.

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