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Nicol, M.J. (2017) The use of impedance measurements in the electrochemistry of the dissolution of sulfide minerals. *Hydrometallurgy*, 169. pp. 99-102.

<http://researchrepository.murdoch.edu.au/id/eprint/35084/>

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Accepted Manuscript

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PII: S0304-386X(16)30755-1
DOI: doi: [10.1016/j.hydromet.2016.12.013](https://doi.org/10.1016/j.hydromet.2016.12.013)
Reference: HYDROM 4491
To appear in: *Hydrometallurgy*
Received date: 17 October 2016
Revised date: 9 December 2016
Accepted date: 16 December 2016



Please cite this article as: Michael J Nicol , The use of impedance measurements in the electrochemistry of the dissolution of sulfide minerals. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Hydrom(2016), doi: [10.1016/j.hydromet.2016.12.013](https://doi.org/10.1016/j.hydromet.2016.12.013)

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The Use of Impedance Measurements in the Electrochemistry of the Dissolution of Sulphide Minerals.

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Abstract

Capacitance measurements made in previous studies of the anodic behaviour of chalcopyrite in dilute sulfuric acid solutions have been compared. The results have shown considerable variability in both the absolute value of the capacitance as well as variations with potential. A limited study has been made of such capacitance measurements largely with the aim of establishing the effect of non-steady-state conditions on the capacitance. Potentiostatic measurements at a carefully selected frequency have shown that there is significant variation of the capacitance with time that follows similar trends to the measured current densities. The capacitance decreases with increasing potential in the range 0.40V to 0.95V but increases rapidly with increasing potential above 1.0V. The results of the previous capacitance measurements have been questioned due to a combination of a lack of steady-state conditions and the choice of the measurement frequency. The present results have been interpreted in terms of a previously published model that is similar to the well-known de-alloying of some binary alloys.

Keywords: chalcopyrite; electrochemistry; anodic behaviour; capacitance; semiconductor

1. Introduction

In recent years, the use of EIS (Electrochemical Impedance Spectroscopy) has become a more generally applied technique by many authors (Hiroyoshi et al, 2004; Viramontes-Gamboa et al, 2006; Ghahremaninezhad et al, 2010; Crundwell, 2014; Crundwell et al, 2015; Olvera et al, 2016) in probing the electrochemistry of the mixed-potential model for the leaching of conductive sulphide minerals, particularly chalcopyrite. As will be shown below, the results of these studies have been variable and the conclusions therefore not convincing. In particular, the interpretation in terms of the semiconducting properties of chalcopyrite as reflected in Mott-Schottky plots should be questioned given the variability and the quality of the measurements on which they are based.

The availability of software that enables the calculation of parameters such as the double-layer capacitance and corrosion rates in addition to the modelling of data such as that presented in Nyquist plots in terms of equivalent circuits has resulted, in this authors view, of much speculation surrounding the nature of the surface species and mechanisms involved in the oxidative dissolution of chalcopyrite. This has come about because the investigators have generally failed to recognize the following points.

1. Measuring an EIS spectrum takes time (often many hours depending on the lowest frequency used) even at a single potential. The system being measured must be at steady-state throughout the time required to accumulate the data at many frequencies. A common cause of problems in EIS measurements and interpretation is that the system (as reflected in, for example, the current in a potentiostatic experiment) is changing with time and therefore the normal EIS tools may give inaccurate results and questionable interpretation.

2. Measurement of the interfacial capacitance (generally as a function of potential) using only one frequency will not yield the correct value unless the frequency used is carefully selected to be in the central region of the linear section of a Bode plot for the system. (Darowicki et al, 2006). In this region, the calculated capacitance should be independent of frequency. The use of linear potential sweeps in conjunction with impedance measurements at a fixed frequency should be avoided given the problem of ensuring a steady state at each potential.

It is now well known that the oxidation of chalcopyrite at potentials in the region of the mixed potential observed in the presence of an oxidant such as iron(III) is initially relatively rapid but the rate decays slowly over periods that can exceed 24 hours (Nicol and Zhang, 2017). For this reason the attainment of a steady-state is unlikely over a period of minutes to a few hours, even at one potential. For this reason, this author has avoided the use of EIS techniques in such studies. This short paper will compare data obtained in several published studies under relatively similar conditions. In addition, the results of some careful measurements made in our laboratory are compared with the published data and it will be shown that our data is consistent with a model for the so-called passivation of chalcopyrite in chloride solutions recently published (Nicol and Zhang, 2017).

2. Experimental

The electrode used in this study was fabricated from a pure natural sample from China as described in a recent publication (Nicol and Zhang, 2016, 2017). It was roughly rectangular in shape with an area of 0.4 cm^2 . The sample was established as n-type from the sign of the experimental thermoelectric potential.

Electrochemical measurements were carried out using a standard three-electrode system. Potentials and currents were measured and controlled by a PAR 273A potentiostat in conjunction with an EG&G 5210 lock-in amplifier for the impedance measurements. The silver/silver chloride (3mol/L potassium chloride) reference electrode (0.207 V versus SHE) was separated by a Luggin capillary from the solution in the cell. All potentials shown are relative to the standard hydrogen electrode. A platinum wire was used as the counter electrode. The electrolyte contained 0.3M sulfuric acid and all measurements were made in a thermostatted cell at 25°C. The electrodes were polished with wet 1200 and then 3000 grit carbide paper and thoroughly rinsed before each experiment. The rest or open-circuit potential of the mineral electrode was recorded for a period of 5 minutes after which the potential was stepped to the desired value and the current recorded as a function of time for at least 60 minutes. An AC signal of 4mV was used in the simultaneous impedance measurements. Measurements at various frequencies in the range 0.05 to 10000 Hz were made after polarization at each potential for one hour and the data analysed in terms of Bode plots that showed that a frequency of 300 Hz was suitable for measurement of the capacitance of the electrode. Each point shown in the plots below was obtained in a separate experiment on a freshly polished mineral surface.

3. Results and Discussion

Data from recent publications was extracted from the relevant published curves and is plotted in terms of the measured capacitance of chalcopyrite in dilute sulfuric acid solutions as a function of potential in two ranges as shown in Fig. 1. It is not clear how these measurements were made but it is assumed that in each case the capacitance was obtained from impedance measurements made during a linear

potential sweep in a positive direction. The sweep rate was not specified in all cases. The frequency used in these experiments was 1kHz by Olvera et al (Study 1) , 1kHz and 10kHz by Ghahremaninezhad et al (Study 2) and 100kHz by Crundwell et al (Study 3).

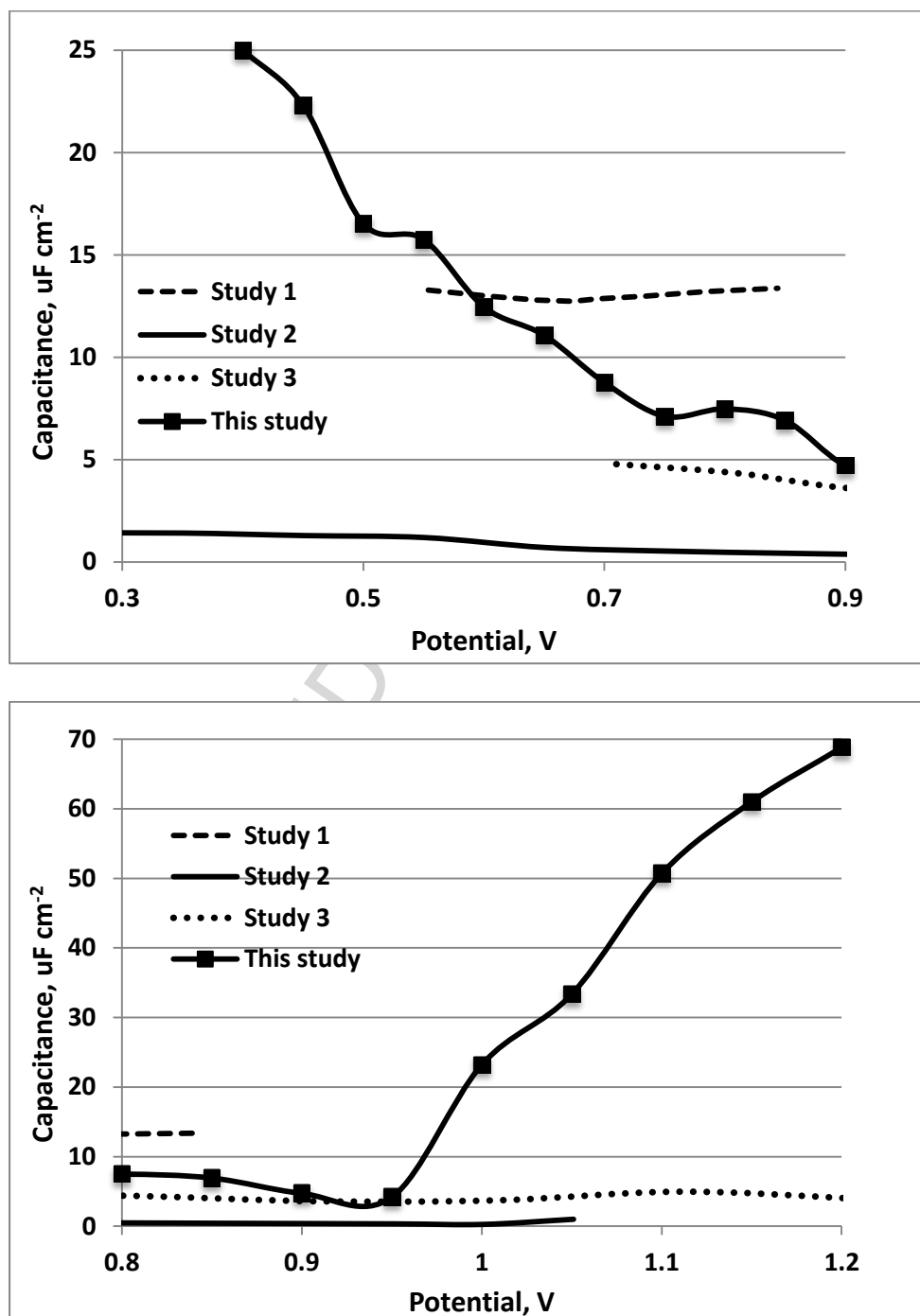


Fig. 1. Variation of the measured capacitance of chalcopyrite electrodes with potential in dilute sulfuric acid solutions at 25°C.

Also shown in Fig. 1 are the measurements made in the present study after the freshly polished electrode was polarized for 1h at each of the potentials shown as points using a frequency of 300Hz (see below).

There are several points to be noted from a comparison of these data (ignoring that from the present study in this instance).

1. In the low potential range (below 0.9V, the measured capacitance differs by an order of magnitude from less than $1\mu\text{F cm}^{-2}$ to about $14\mu\text{F cm}^{-2}$. At potentials above 0.7V (where there is data from all studies), the slope of the trends are small negative with potential with the exception of Study 1. This decrease in capacitance with potential has been interpreted by all authors in terms of the Mott-Schottky relationship for the space charge layer in an n-type semiconductor. The results for Study 1 would suggest a p-type material at potentials above about 0.65V.
2. In the high potential range the above conclusions also apply but, in addition, the data for Study 3 suggests p-type behaviour at potentials from about 1V to 1.1V above which the material apparently reverts to n-type again.
3. With the possible exception of Study 2, the values of the capacitance are considerably greater than those expected for the space-charge layer in a semiconductor but lower than those typical of the Helmholtz double layer in the aqueous phase. Thus, the assumption that the measured values are those of the space charge layer in the solid cannot be made with any certainty.

In order to resolve some of these uncertainties, several measurements were made largely to assess the variation of the measured capacitance of chalcopyrite as a function of time at fixed potentials. The capacitance at selected potentials is shown as a function of time in Fig. 2. At potentials below about 1V, the capacitance decreases

with time and is still decreasing after several hours as shown at a potential of 0.65V in Fig. 3. At higher potentials the transients are more complex but the capacitance still changes significantly with time. The anodic current follows similar trends as shown at a low potential in Fig. 3 and a high potential in Fig. 4. As observed in a recent publication (Nicol and Zhang, 2017) the current does not generally reach a steady-state even after 24 hours at low potentials. Interestingly, the rate of oxidation of iron(II) also decreases with time in a similar fashion in chloride solutions as recently reported (Nicol and Zhang, 2016).

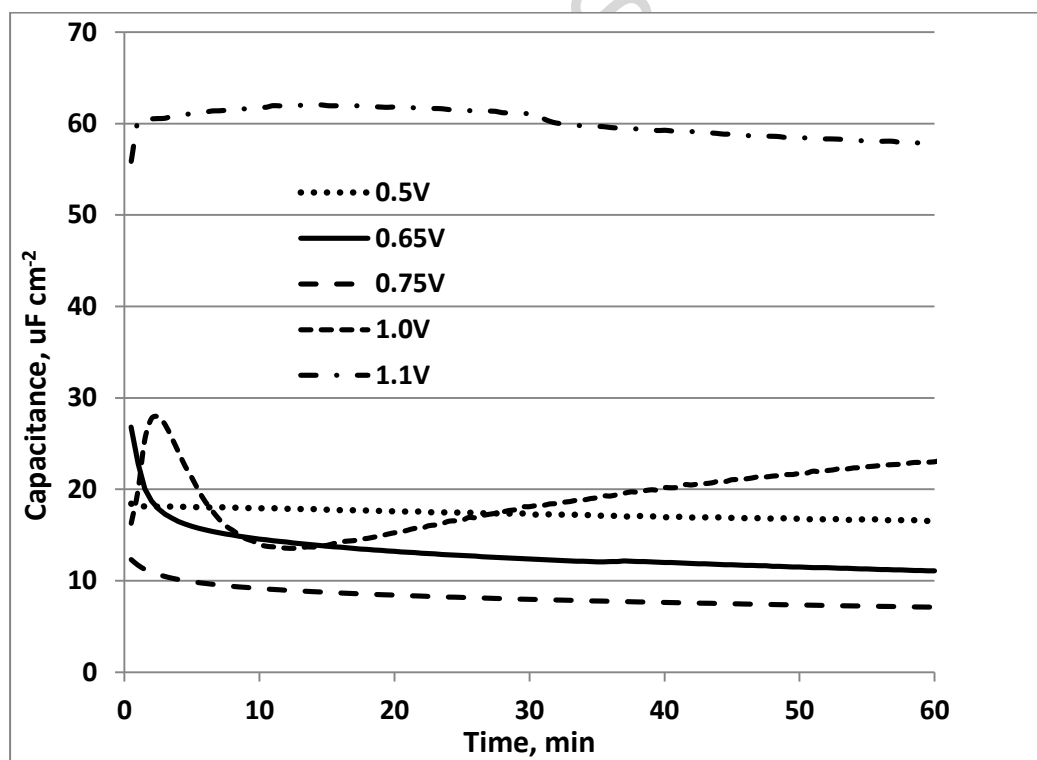


Fig. 2. Variation with time of the capacitance of chalcopyrite at various potentials in dilute sulfuric acid at 25°C.

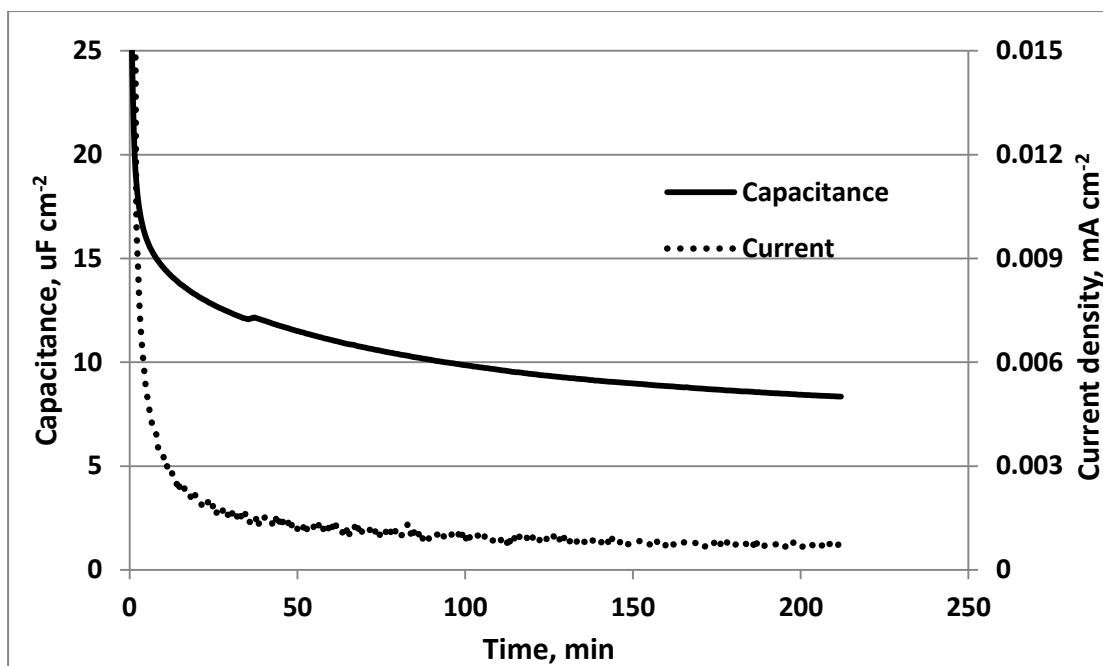


Fig. 3. Comparison of the variation of the capacitance and the anodic current density with time at 0.65V.

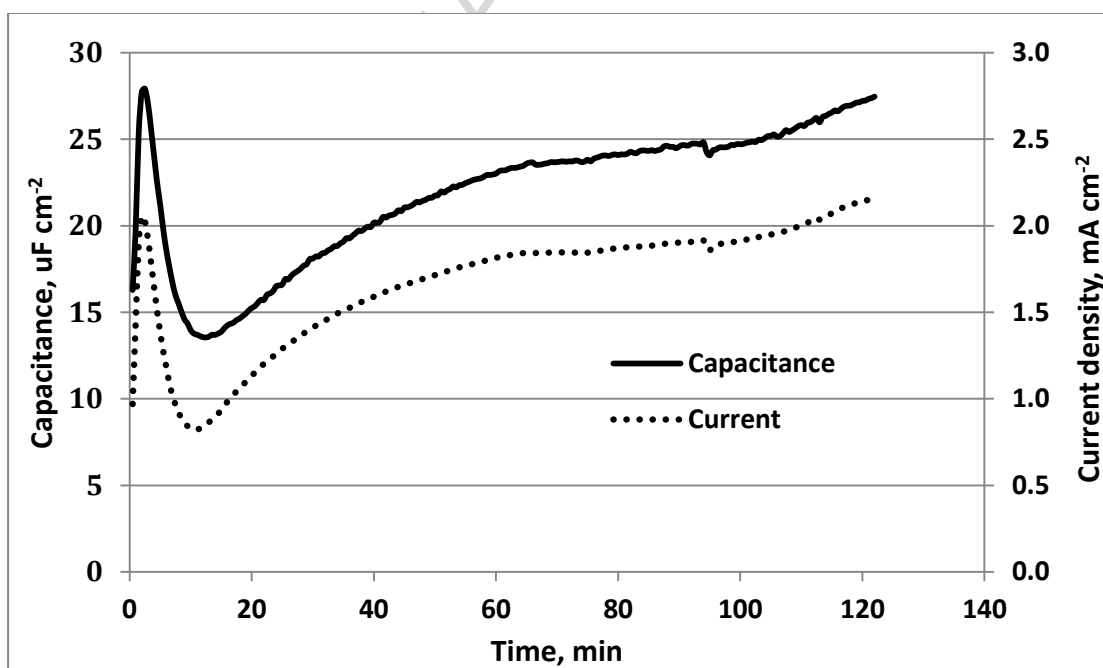


Fig. 4. Comparison of the variation of the capacitance and the anodic current density with time at 1.0V.

Thus, the measured capacitance is a function not only of the potential but also of time and data obtained by simply measuring the capacitance or the impedance during a

sweep of the potential reveals the effects of both potential and time. Recognizing that steady state is only partially achieved after one hour, the capacitance is shown in Fig. 1 and both the capacitance and current density as a function of potential are plotted in Fig. 5. There is understandably some scatter in the capacitance measurements given that each point represents an experiment with a freshly polished surface with some variability in actual surface area.

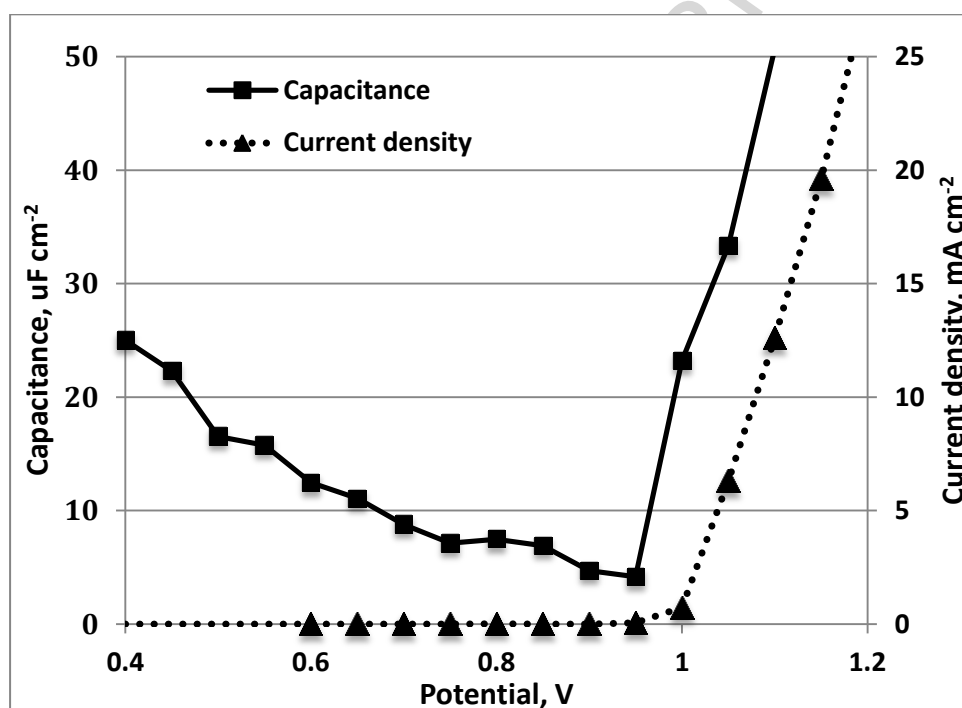


Fig. 5. Comparison of the capacitance and current density after 1h at various potentials for chalcopyrite at 25°C.

At potentials below about 0.95V, the current is low and is cathodic at potentials below about 0.55V. The decrease in the capacitance from 0.4V to 0.95V is approximately linear and the slope significantly greater than that obtained in the previous studies shown in Fig. 1. The steep rise in the capacitance at higher potentials is accompanied by a corresponding rise in the current density in this transpassive potential region. The capacitance attains values in excess of 60 uF cm⁻² at the highest potentials. This value

is typical of the capacitance of the Helmholtz double layer in the solution. Visual observations of the electrode surface (details to be presented in a subsequent publication) showed that at potentials below about 1.0V, the surface became lightly tarnished after extended oxidation. However, as the current density increased above 1.0V, a dark grey/black layer became obvious after about 30 minutes. Extended oxidation at potentials above 1.1V resulted in the slow removal of this layer revealing a pitted golden chalcopyrite surface with no obvious surface layer.

The variation of the capacitance with frequency was measured after 1h at 0.4V and at 0.85V and the results shown as Bode plots in Fig. 6. Lines of the theoretical unit slope are also shown.

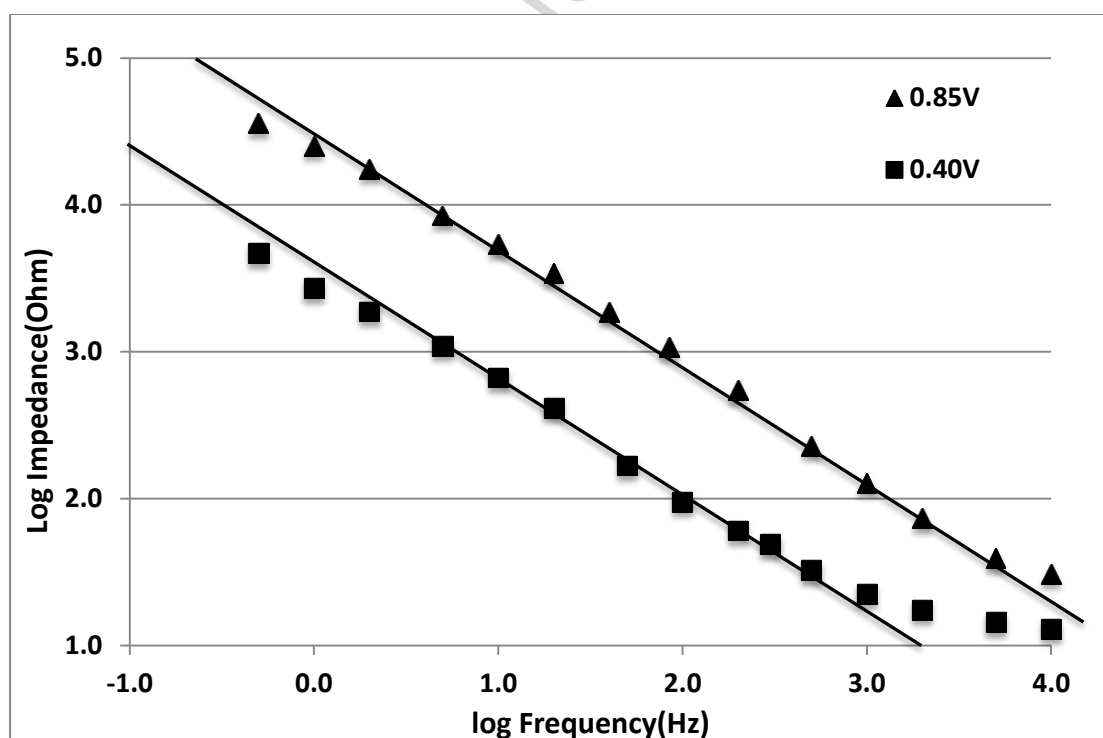


Fig. 6. Bode plots for chalcopyrite at two potentials.

These plots can be used to establish that the use of frequencies outside of the linear regions of unit slope (about 5 to 500 Hz) will not yield accurate estimates of the capacitance (Darowicki et al, 2006). The use of a frequency of 1kHz would probably

provide reasonably accurate data but values of 10kHz and, especially, 100kHz, would not be suitable as, at these frequencies, the impedance is dominated by the uncompensated resistance of the series combination of the solution and solid electrode resistance and is insensitive to the capacitance. Thus, the data obtained in Study 3 is unreliable as is that for Study 2 at 10kHz.

As shown in Fig. 3, at potentials relevant to the oxidative leaching of chalcopyrite under ambient conditions, the current (and therefore the rate) decreases with time over an extended period. Similar results were obtained in an extensive study in chloride solutions (Nicol and Zhang, 2017). These results were interpreted in terms of the formation of a less anodically reactive but very thin “passivation” layer on the surface of the mineral as a result of the selective removal of iron in a process similar to the well-known de-alloying of some binary alloys. This layer will continue to grow in thickness with time resulting in decreasing currents at fixed potentials. The effect of increasing the potential in this region below about 1.0V is relatively minor with increases in current density and therefore probably thicker layers at the higher potentials. The rate-determining step under these conditions is suggested as being solid-state diffusion of iron and possibly also some copper to the surface. The formation of this thin layer (often labelled as a polysulfide) will result in a capacitive layer between the solution and the bulk chalcopyrite similar to that of an oxide layer on a metal. As the thickness of this layer increases, the capacitance associated with it will decrease (capacitance is inversely proportional to the distance of separation of charge) as shown by the results in Fig. 5.

At the critical potential of about 1.0V, this layer is not stable and rapid oxidation reflected in significantly increased current occurs with the formation of visible sulfur on the surface. The thickness of the layer decreases with both time and increasing

potential as the layer is oxidized resulting in a rapidly increased capacitance (the insulating sulfur layer does not appear have the morphological and electronic properties necessary to influence either the capacitance or the current). After extended periods at higher potentials, the sulfur appears to be oxidised and a clean but pitted chalcopyrite surface is restored. The observed capacitance is now that primarily of the Helmholtz layer in the aqueous phase.

These observations are difficult to reconcile with a model in which the semiconducting properties of chalcopyrite dominate the electrochemistry and dissolution behaviour for several important reasons.

1. The large differences in the measured capacitance and its variation with potential in the previous studies are difficult to explain as being simply due to variability in the properties of the mineral samples used.
2. The data obtained in the previous studies have been shown to be largely unreliable because of the combined effects of the absence of steady-state conditions and incorrect choice of measurement frequency. This has resulted in very different values and trends with potential for the capacitance.
3. With the possible exception of Study 2 at 1KHz, the values of the capacitance are higher than could be expected for a semiconducting material.
4. The slow changes (over many hours) of the capacitance are not typical of semiconducting materials that generally respond much more rapidly.

These considerations taken in conjunction with many additional observations on the reactivity of the mineral noted in previous publications must cast considerable doubt on the validity of claims that the “passivity” of chalcopyrite is not due to the nature of the ill-defined but generally accepted polysulfide layer but are due to the semiconducting properties of the mineral itself. The only experimental evidence in

support of the semiconductor theory has been i) apparent photocurrents at chalcopyrite, ii) capacitance measurements and iii) limiting (saturation) anodic currents (Crundwell et al, 2015). The results of (i) were recently shown (Nicol, 2016) to be in doubt given that thermal- and not photo-effects could explain the results while the present study has cast considerable doubt on the validity of the capacitance measurements. The occurrence of saturation currents will be addressed in a subsequent more general paper on the anodic behaviour of chalcopyrite that will include results from other published work that also do not show such saturation effects. Finally, apparent agreement between the results obtained using questionable data and multi-parameter semiconductor models as justification (Crundwell, 2014; Crundwell et al, 2015) for the semiconductor theory cannot be accepted as validity for such models.

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Highlights

Capacitance measurements from previous studies of the anodic behaviour of chalcopyrite in dilute acid solutions have been compared.

The results show variability in both the value of the capacitance as well as its variation with potential.

Potentiostatic measurements at various potentials have shown that there is significant variation of the capacitance with time.

The capacitance decreases with increasing potential in the range 0.40V to 0.95V but increases rapidly with increasing potential above 1.0V.

The results have been interpreted in terms of a published model that is similar to the de-alloying of some binary alloys.