

# Electrochemical Determination of Roughness of Silver Electrode Surface

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Neste trabalho diferentes métodos eletroquímicos "in situ" foram utilizados para analisar aspectos na determinação da área superficial de eletrodos de prata polida e eletrodepositada. Esses métodos, baseados em voltametria cíclica, foram usados para: (a) determinar a carga de redução de óxidos formados a diferentes potenciais de inversão; (b) determinar a pseudo-capacitância da dupla camada elétrica; (c) realizar a deposição de cádmio sob regime de subtensão (upd). O fator de rugosidade obtido por esses métodos foram então relacionados com o deslocamento do ângulo de fase observado em medidas de impedância a.c. Os experimentos foram conduzidos em solução aquosa pura de KF 0,1 M para os experimentos (a) e (b), e em uma mistura de soluções com a seguinte composição:  $\text{CdSO}_4 10^{-2} \text{ M} + \text{Na}_2\text{SO}_4 0,5 \text{ M} + \text{H}_2\text{SO}_4 10^{-2} \text{ M}$ , para os experimentos de upd ((c)). Os resultados obtidos pelas diferentes técnicas são muito similares, confirmando a equivalência entre elas para a determinação da área superficial real de eletrodos sólidos. Uma dependência linear do deslocamento do ângulo de fase observado em medidas de impedância a.c. com a rugosidade de eletrodos foi observada.

In this work different *in situ* electrochemical methods were used to analyze the features in the determination of the superficial area of polished and electrodeposited silver electrodes. These methods, based on cyclic voltammetry, were used to: (a) determine the reduction charge of oxides formed at different inversion potentials; (b) determine the pseudo-capacitance of the electrical double layer; (c) perform the underpotential deposition of cadmium. The roughness factor obtained by these methods was then correlated with the phase angle shift observed from the a.c. impedance spectroscopy. The experiments were performed on pure 0.1 M KF aqueous solution for the experiments (a) and (b), and on a mixed solution with the following composition:  $10^{-2} \text{ M CdSO}_4 + 0.5 \text{ M Na}_2\text{SO}_4 + 10^{-2} \text{ M H}_2\text{SO}_4$ , for the upd experiments ((c)). The results obtained with these different techniques were very similar confirming their equivalence to determine the real surface area of solid electrodes. A linear dependence of the phase angle shift from a.c. impedance measurements with the electrode roughness was observed.

**Key words:** surface area; roughness factor; electrochemical methods; phase angle shift.

## Introduction

Many publications<sup>1-3</sup> had focused on a very important aspect in electrochemical studies with solid electrodes: *the determination of the real surface area*. In one of these publications, the author suggested that the most appropriate method for a surface area determination was the one that best approaches the experimental situation to which the area determined is to be applied.<sup>3</sup> In 1991, Trasatti and Petrii<sup>4</sup> dedicated a very didactic paper to this subject where presented a review of methods applying *in-situ* and *ex-situ* techniques to determine the real surface area.

One of the methods pointed out by Trasatti and Petrii<sup>4</sup> is *cyclic voltammetry*. This method can be used in three different ways:

(1) To calculate the charge involved in the reduction of surface oxides generated during consecutive potential sweeps beginning at the same potential but with increasing anodic inversion potential. A plot relating to the reduction charge of these oxides with the inversion potential usually presents straight lines with different slopes which in turn are related to the number of electrons transferred for the formation of the different kinds of oxides or hydroxides. The charge related to the first change in the slope is attributed to a reduction of the first metal hydroxide monolayer and, therefore, can be associated with its electroactive surface area. This procedure has been applied mainly for palladium electrodes<sup>5</sup>;

(2) For metals showing a well-defined double layer region it is possible to estimate a pseudo-capacitance through the

dependence of the capacitive current with the sweep rate. In this case the surface area can be calculated from the equation<sup>6</sup>:

$$\frac{C}{A_s} = \frac{\Delta i}{\Delta E/t} \quad (1)$$

where  $C$  is the pseudo-capacitance of the double layer which must be compared to the one corresponding to a smooth surface electrode (e.g.,  $0.16 \text{ F m}^{-2}$  for mercury<sup>6</sup> and  $0.25 \text{ F m}^{-2}$  for nickel<sup>7</sup>),  $\Delta i$  is the current variation with the sweep rate ( $\Delta E/t$ ) and  $A_s$  is the surface area.

(3) Another usual method is the *underpotential deposition of metals*. In this technique, the first monolayer of some metals deposited on a foreign substrate requires a potential more anodic than the Nernst potential of the pair  $M/M^{Z+}$ . Arvia and co-workers<sup>8</sup> used the underpotential deposition of cadmium to determine the surface area of highly porous silver electrodes. They compared the charge densities obtained for the formation of a lead or cadmium monolayer on platinum with those obtained on electrodeposited silver. However, the value used for the charge density on platinum (i.e.  $4.20 \text{ C m}^{-2}$ ) was not compatible with those reported earlier of  $0.88 \text{ C m}^{-2}$  for lead<sup>9</sup> and  $3.19 \text{ C m}^{-2}$  for cadmium<sup>10</sup>, given significative errors on the area determination of silver.

On the other hand, the surface roughness of solid electrodes, usually associated with the fractal dimensions of the surface, has been the subject of several communications correlating this factor with the phase angle shift observed on a.c. impedance measurements<sup>11-13</sup>. On a solid electrode, in a potential region with no faradaic processes, an a.c. impedance measurement can be interpreted by an electronic analog containing one resistor in series with a constant phase element (CPE). Thus, the total impedance ( $Z$ ) of the metal/solution interface is usually expressed as:

$$Z = R_s + \frac{R_s^{\alpha}}{(j\omega C_d)^{1-\alpha}} \quad (2)$$

where  $R_s$  is the solution resistance,  $C_d$  the capacitance of the double layer and  $\alpha$  a fitting parameter which has values of 0.5 and 1.0 for porous and smooth surfaces, respectively. Using this procedure, Rammelt and Reinhard<sup>12</sup> studied the applicability of a CPE to estimate the roughness of rotating polycrystalline iron electrodes in contact with  $\text{H}_2\text{SO}_4$  solution. They observed that the fractional CPE exponent is a function of the fractal dimension ( $D$ ) represented by  $\alpha = 1/(D - 1)$ , independently of the metal nature.

In the present communication, polished silver electrodes had their surface area determined by voltammetry for oxide reduction, pseudo-capacitance determination and underpotential deposition (upd) of cadmium. As the roughness factors obtained from the application of these different methods resulted in equivalent values, for surfaces of electrodeposited silver on a silver substrate, at different deposition current densities, the determination of the charge due the oxide reduction was the only method used. The roughness factor values obtained in that way, were then correlated with the phase angle shift resulting from impedance measurements. The impedance measurements were performed at four different electrode potentials in the double layer region (0, -0.3,

-0.5 and -0.7 V) in a 0.1 MKF aqueous solution and analyzed with the use of an equivalent circuit containing a constant phase element (CPE), as mentioned before<sup>11,12</sup>.

## Experimental

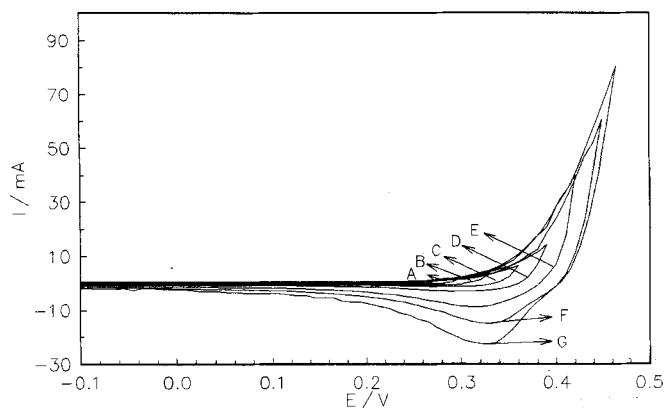
The preparation of the silver electrodes involved the melting of a silver wire (Degussa 99.995%) in a spectroscopic graphite crucible using an inductive furnace. The crucible containing pieces of the silver wire was inserted in a quartz tube and submitted to vacuum for 30 minutes before melting. The resulting silver cylinder (1 cm length and 0.32 cm diameter) had one of its faces mechanically polished with emery paper (from 400 to 1500) followed by alumina (1, 0.5, 0.3 and 0.1  $\mu\text{m}$ ). Between each step of the polishing process the silver cylinder was carefully washed with purified water using together an ultrasonic bath in order to remove residual polishing particles more effectively. Before each electrochemical measurement the silver cylinder was also submitted to a chemical polishing treatment consisting of: (a) immersion in concentrated sulfuric acid for 10 minutes, washing with water and drying with nitrogen; (b) dipping into concentrated perchloric acid followed by immediate transference to a 50/50 (v/v) mixture of 4 M  $\text{CrO}_3$  and 0.6 M  $\text{HCl}$  for 1 minute; (c) washing with water followed by immersion into a becker with concentrated ammonia for 3 minutes; d) finally, washing with water and transference to the cell with a water drop hanged on the tip to prevent contamination by laboratory atmosphere.

Electrodeposited silver electrodes were prepared after the same treatment described above using a solution of silver nitrate (35 g/l), ammonium hydroxide (7 g/l) and ammonium sulfate (160 g/l). For all electrodeposits the charge was kept constant at  $0.12 \mu\text{C}$  with the electrodeposition current density varying as: 1.3, 4.0 and  $4.8 \text{ A m}^{-2}$ . In such a way one can expect electrodeposits with surface roughness increasing with the current density. Also the electrodeposited silver electrodes were washed exhaustively with water and transferred to the cell with a water drop hanged on the tip.

This water drop hanged on the electrode tip not only is used to avoid contamination but also allows the formation of a meniscus between the solution and the electrode surface. The meniscus technique described in the literature<sup>3</sup> was used in all experiments including in the electrodeposition step. For all experiments, performed at  $25 \pm 1^\circ\text{C}$ , the counter electrode was a silver spiral and the reference was a saturated calomel electrode (SCE).

The 0.1 MKF solutions used in the a.c. impedance experiments were prepared with potassium fluoride (Merck Suprapur), treated by heating at  $300^\circ\text{C}$  under vacuum and Milli-Q water. The sodium sulfate, cadmium sulfate and sulfuric acid (all Merck P.A.) solutions were prepared with Milli-Q water. The solutions were deaerated with nitrogen purified in a tubular furnace with copper pellets and circulated through two consecutive traps containing molecular sieves of different sizes.

The cyclic voltammetry and upd experiments were performed using a potentiostat/galvanostat PARC 273 controlled by the PARC M270 software and a X-Y recorder HP 7046B. The a.c. impedance measurements were carried out using a system including a potentiostat/galvanostat PARC 273, a lock-in amplifier PARC model 5206, a personal com-

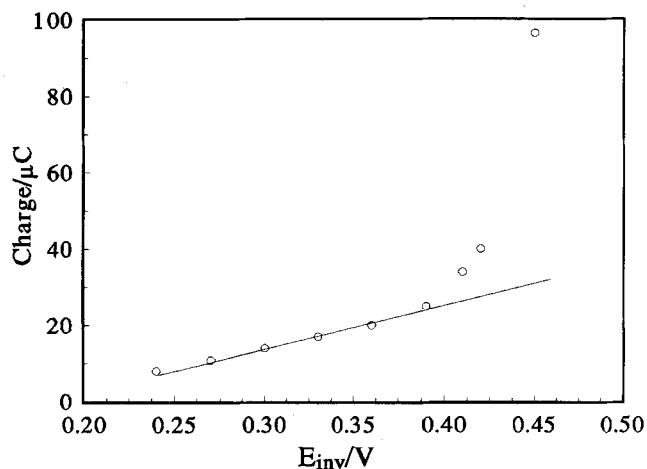


**Figure 1.** Cyclic voltammograms for polished silver electrode in 0.1 M KF aqueous solution. Scan rate 0.05 V/s. Inversion potential: (a) 0.3, (b) 0.34, (c) 0.36, (d) 0.40, (e) 0.42, (f) 0.44 and (g) 0.46 V.

puter AT-386 and the software PARC M378. The impedance spectra were obtained in the frequency range of 5 Hz to 20 kHz using a alternated potential of  $1 \times 10^{-2}$  V p.p. and analyzed by an appropriate software developed by R. MacDonald<sup>16</sup>.

## Results and Discussion

**Cyclic Voltammetry:** a) *Reduction of surface oxides.* Figure 1 shows steady state cyclic voltammograms for polished silver on 0.1 MKF aqueous solution at  $0.05 \text{ V s}^{-1}$ , for different inversion potential values. One can observe that the cathodic peak occurring from approximately 0.3 V increases when the inversion potential is made more positive. The charge calculated from the area under the curve shows a linear dependence



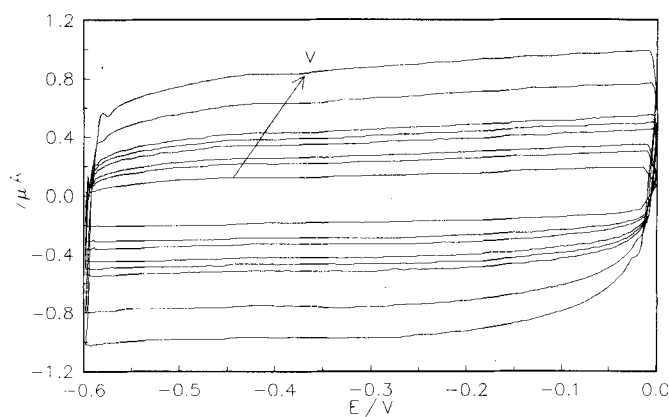
**Figure 2.** Reduction charges of the silver oxides grown in the anodic scan as a function of the inversion potential from the voltammograms in Figure 1.

with the inversion potential until approximately 0.4 V followed by an exponential dependence. The linear increase of the charge with the inversion potential corresponds to a monolayer formation of AgOH and Ag<sub>2</sub>O, whereas the potential region where the exponential increase occurs corresponds to silver dissolution ( $E_{rev} \approx 0.45 \text{ V vs SCE}^{14}$ ), which increases the electrode area. In Figure 2 is shown the calculated charge (calculated by the integration of the cathodic branch of each voltammogram and considering the straight line in the potential range of -0.1 to 0.1 as the baseline) from the reduction peaks of silver oxide grew during the sweeps present in Figure 1, as a function of the inversion potentials. One can observe two distinct regions in Figure 2: one linear and other non-linear. The point where the experimental curve loses the linearity is around 0.4 V and the charge associated to this potential was determined as being  $25 \mu\text{C}$ . As the oxidation reaction of the silver surface involves one electron per Ag atom, a complete monolayer of either AgOH or Ag<sub>2</sub>O consumes approximately  $2.10 \text{ C m}^{-2}$  (as calculated by Tang and Furtak<sup>17</sup>). So, the real surface area of the polished silver electrode is  $11.9 \times 10^{-6} \text{ m}^2$  which compared with the geometric area of the electrode of  $8.0 \times 10^{-6} \text{ m}^2$ , results in a roughness factor of this electrode of 1.49.

The evaluation of the exact points where the linear region ends and begins the exponential one in Figure 2 is very difficult mainly because of the overlapping of different processes, as pointed out by Trasatti and Petrii<sup>4</sup>. In the present analysis no efforts were made to determine any double layer effects.

b) *Pseudo-capacitance determination.* Trasatti and Petrii<sup>4</sup> mentioned some limitations for the use of this method as the restrict use of it to a large surface area and porous electrodes but mainly when it is applied to oxide electrodes. Silver has a large double layer region and in the selected potential range there is no oxide formation. On the other hand, because this method involves a non-destructive process of the surface it was applied to determine the real area of all the electrodeposited electrodes.

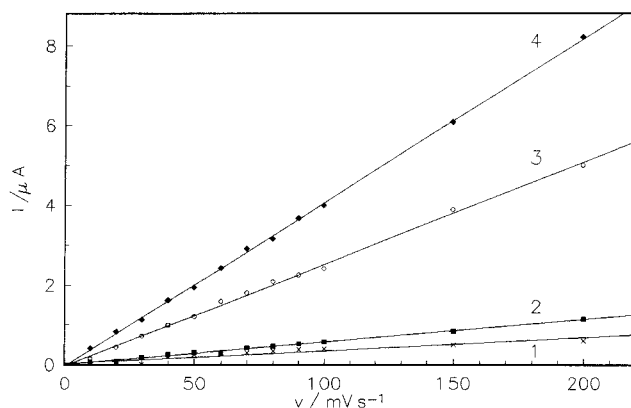
Figure 3 shows cyclic voltammograms for different sweep



**Figure 3.** Cyclic voltammograms for polished silver electrode in 0.1 M KF aqueous solution in a non faradaic potential range at the following scan rates: (1) 0.01, (2) 0.03, (3) 0.04, (4) 0.07, (5) 0.08, (6) 0.10, (7) 0.15 and (8) 0.20 V/s.

**Table 1.** Electroactive surface area and roughness factor for several silver electrodes calculated with the pseudo-capacitance method.

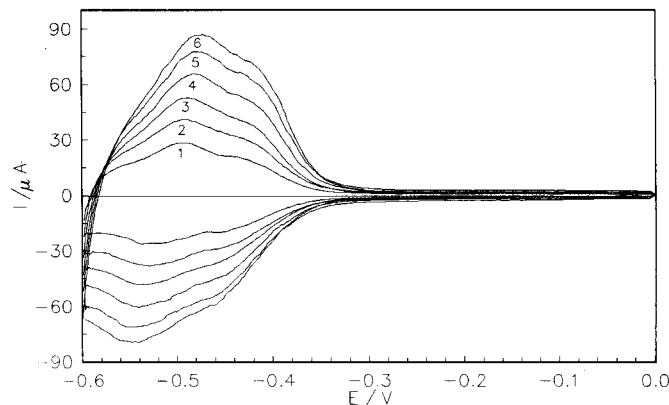
Ag Electrode	$i_{dep}$ A.m <sup>-2</sup>	Surface area 10 <sup>4</sup> x m <sup>2</sup>	Roughness factor
Polished	---	0.120	1.50
ED1	1.3	0.298	3.72
ED2	4.0	0.988	12.35
ED3	4.8	1.60	20.00



**Figure 4.** Anodic current at -0.3 V as a function of scan rate for the voltammograms of Figure 3. Kind of electrodes: (1) polished silver, (2) ED1, (3) ED2 and (4) ED3.

rates on polished silver electrode in contact with a 0.1 M KF aqueous solution, in a potential range where no faradaic process occurs. In order to calculate the total pseudo capacitance of this interface following the equation 1, the potential of -0.3 V was chosen. The value of the anodic current at this potential was plotted against the sweep rate for the different types of electrodes, as shown in Figure 4. The straight lines presented in Figure 4 make evident the capacitive behavior of the interface, as the equation 1, and they are related to the following electrodes: (1) polished silver; (2) first electrodeposit (at deposition current density,  $i_{dep}$ , of 1.3 A m<sup>-2</sup>); (3) second electrodeposit ( $i_{dep} = 4$  A m<sup>-2</sup>); (4) third electrodeposit ( $i_{dep} = 4.8$  A m<sup>-2</sup>). Considering a value of 0.25 F m<sup>-2</sup> for the polished silver pseudocapacitance<sup>15</sup>, it is possible to calculate the active area of the electrodes from equation 1. These values are presented in Table where one can observe that there is a linear increase of the slopes with  $i_{dep}$  and therefore of the electrode surface area. The difference in the values of the roughness factor observed between this method (1.5) and the preceding one (1.49) is around 1% which can be considered very small because the imprecisions that are inherent to the determinations from Figure 2.

c) *Underpotential Deposition of Cadmium* As mentioned



**Figure 5.** Steady-state cyclic voltammograms for the underpotential deposition of cadmium on polished silver electrode from the aqueous solution: 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.01 M H<sub>2</sub>SO<sub>4</sub> + 0.01 M CdSO<sub>4</sub>. Scan rate 0.05 V/s.

**Table 2.** Anodic charge associated with one monolayer of adsorbed cadmium on polished Ag electrode at several scan rate.

Scan Rate V s <sup>-1</sup>	Desorption Charge C m <sup>-2</sup>
0.10	0.3453
0.20	0.3426
0.30	0.3308
0.40	0.3326
0.50	0.3349
0.60	0.2922

before this method is one of the most used to determine the silver surface area. However there are limitations as correction for double layer charging and precise identification of the end point for the metal adsorption, as pointed out by Trasatti and Petrii<sup>4</sup>. The underpotential deposition of a cadmium monolayer on polished silver presents two cathodic and two anodic peaks, like those already reported in references<sup>8,17</sup>, as shown in Figure 5, at 50 mV/s, in a solution with the composition: 0.01 M CdSO<sub>4</sub> + 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.01 M H<sub>2</sub>SO<sub>4</sub>. The deposition and redissolution charges, in the potential range between -0.2 and -0.6 V, are equivalent and the values of the redissolution ones are presented in Table. The constancy observed in the redissolution charge value with respect to the sweep rate makes sure that, also at fast sweep rate, the cadmium monolayer is complete. The mean value calculated (up to 0.50 V s<sup>-1</sup>) was 33.72 μC and the transformation of this value to electroactive area involves a comparison with this monolayer properties on a well know

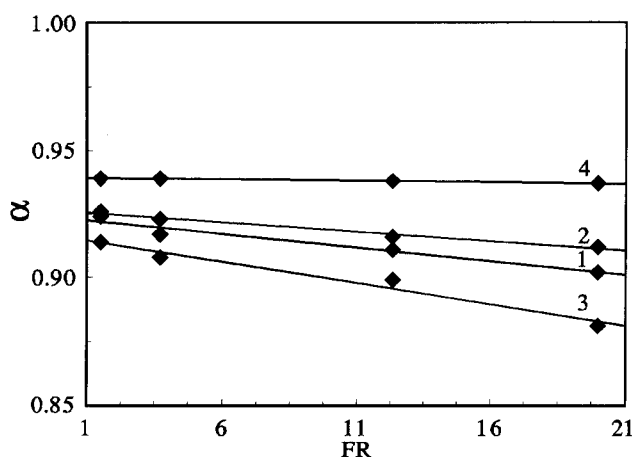
**Table 3.** Phase angle shift ( $\alpha$ ) values from a.c. impedance measurements for different values of applied potential and different roughness of silver electrodes. Roughness factor (RF) obtained by pseudo-capacitance determinations.

Ag electrode	polished	ED 1	ED 2	ED 3
RF	1.50	3.731	2.35	20.00
E = 0.0 V	0.924	0.917	0.906	0.902
E = -0.3 V	0.926	0.923	0.912	0.912
E = -0.5 V	0.914	0.908	0.899	0.881
E = -0.7 V	0.939	0.939	0.938	0.937

substrate, as platinum. In the system Pt / Cd<sub>ads</sub><sup>10</sup>, each Cd atom occupies an active site on the surface and the number of electrons transferred is 1.55. In this case, the charge density equivalent to a monolayer is 3.19 C m<sup>-2</sup>. Supposing that the Ag/Cd<sub>ads</sub> system has analogous behavior because the crystallographic radii for Ag, Pt and Cd atoms are very close<sup>8</sup>, the calculated value of 33.72  $\mu$ C corresponds to an active area of 10.5  $\times 10^{-6}$  m<sup>2</sup> and consequently to a roughness factor of 1.31. This value of the roughness factor is approximately 10% lower than the others observed by the preceding methods but one can consider them in agreement. The limitation of this method is its destructive characteristic since the removal of cadmium atoms from the surface might also remove some silver atoms perhaps changing the surface morphology.

d) *Correlation between Surface Area and Phase Angle Shift.* When a.c. impedance measurements are performed on a perfectly smooth surface, in a range of potential where no faradaic processes occur (double layer region), the Nyquist plot (in phase, Z'', versus out phase, Z', impedance component plots) is a straight line parallel to the imaginary axis with an intercept at Z'' = 0 corresponding to the value of R<sub>S</sub>, the

solution resistance. However, in the case of solid electrodes that have inherent roughness, the straight line is still obtained but presenting a deviation from the parallelism to the imaginary axis called the phase shift<sup>13</sup>. As mentioned before, this phase angle shift has been essentially attributed to the magnitude of the roughness factor<sup>11-13</sup> but a clearly established relation between them is still lacking. As mentioned in an early section, the parameter values of the electronic circuit equivalent to the silver / 0.1 M KF solution interface were determined by an iterative program which makes the best non-linear fitting with the experimental data. In Table 3 the values of  $\alpha$  obtained by this fitting method are presented for the different values of applied potential and the different kind of prepared surfaces. As expected, the values of  $\alpha$  decreases when the surface becomes more rough and, as observed for gold<sup>18,19</sup>, there is a dependence of  $\alpha$  with the applied potential. To make these clear, the values of  $\alpha$  are listed with the roughness factor in Table 3 for different values of applied potential. Taking into account the reduced number of points and the low range of roughness of the silver electrodes, one can suppose a linear dependence between the phase angle shift and RF, as shown in Figure 6 for the different electrode potentials. Using this plot to extrapolate the value of  $\alpha$  when FR = 1, the values obtained are very close with a small dependence with the applied potential. However for a smooth surface, which corresponds to FR = 1, the expected value of  $\alpha$  is 1. Two points mentioned by Trasatti and Petri<sup>4</sup> about the roughness and heterogeneity concepts perhaps can explain the behavior observed in Figure 6. First of all, the commonest example of a heterogeneous surface is a polycrystalline one because the periodicity of distribution of atoms differs from place to place and second, a heterogeneous surface may be ideally smooth. So, one can interpret the difference observed for FR = 1 and the expected value of  $\alpha$  as an effect of the heterogeneity of the silver polycrystalline structure and concluded that the phase angle shift observed at the a.c. impedance measurements, does not just reflect the roughness of the surface but also has an intrinsic contribution of the metal heterogeneity.



**Figure 6.** Phase angle shift ( $\alpha$ ) from a.c. impedance measurements as a function of the roughness factor (FR) obtained by pseudo capacitance determinations. The values of potential used to determine are: (1) 0.0, (2) -0.3, (3) -0.5 and (4) -0.7 V.

## Conclusions

In this work the comparison of different in situ methods usually applied to estimate the real surface area of electrodes showed that they give equivalent results in the case of polished silver surfaces. Silver is a good metal to perform the comparison because it presents a large double layer region, it is a suitable substrate for underpotential deposition of cadmium atoms, it is easy to polish to a mirror like finishing, and it is quite stable in contact with the electrolytic solutions used in this work. From the limitations pointed out by Trasatti and Petri<sup>4</sup> about the methods to determine real surface area of electrodes the most important is that the method for the area determination must be performed under conditions close to that one will performed the main electrochemical measurements. So, it is possible to conclude that cyclic voltammetric method applied to pseudo-capacitance determinations is the most reliable when, for instance, a.c. impedance measurements will be taken in the double layer region.

Another interesting point resulting of this work, is that the phase angle shift observed with a.c. impedance measurements on solid electrodes is not only due the roughness factor.

So, it is possible to write:  $\alpha = \alpha_R + \alpha_H$  where  $\alpha_R$  is the roughness and the  $\alpha_H$  the heterogeneity contribution for the total value of  $\alpha$ . The total value of  $\alpha$  is a function of the applied potential, nature and bulk concentration of the species in the solution, as showed for gold<sup>18,19</sup>. However, the value of  $\alpha_H$  seems to be a function of the metal nature, its previous history, which involve different surface treatment, and the applied potential. On the other hand,  $\alpha_R$  is a function of the real area, the electroactive species present in the system and also of the applied potential.

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