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Removal of Cd^{2+} Ion from Diluted Aqueous Solutions by Electrodeposition on Reticulated Vitreous Carbon Electrodes

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A eletrodeposição do íon Cd^{2+} foi investigada em soluções aeradas de ácido sulfúrico-sulfato de potássio em pH 4,8. Sob condições potenciostáticas, usando eletrodos de carbono vítreo reticulado (CVR) de 30, 60 e 100 poros por polegada (ppp), uma elevada eficiência de remoção foi obtida para soluções contendo 5 e 10 mg L^{-1} de íon Cd^{2+}, na faixa de potenciais entre –0,90 e –1,10 V. Neste intervalo, a eletrodeposição do cádmio é controlada por transporte de massa e a concentração de íon Cd^{+2} varia exponencialmente com o tempo, seguindo uma cinética de pseudo-primeira ordem. Para a concentração 10 mg L^{-1} de íon Cd^{2+} e usando o eletrodo de 30 ppp, as eficiências de corrente e de remoção determinadas foram, respectivamente, 45% e 96%, após 30 minutos de eletrólise a –0,90 V, enquanto para 60 ppp foram encontrados 33% e 99%, respectivamente. A voltametria de redissolução anódica com eletrodo de gota pendente de mercúrio foi empregada para monitorar a concentração do íon Cd^{2+} após cada experimento de eletrodeposição.

The electrodeposition of Cd^{2+} ion was investigated in pH 4.8 sulfuric-sulfate solutions in the presence of dissolved O_2. In potentiostatic conditions, using reticulated vitreous carbon (RVC) electrodes of 30, 60 and 100 pores per inch (ppi), high removal efficiency values were achieved in the potential range from –0.90 to –1.10 V for solutions containing 5 and 10 mg L^{-1} of Cd^{2+} ion. In this potential range, Cd electrodeposition is a mass transport controlled reaction and the concentration of the metallic ion decays exponentially with time following a pseudo-first order kinetics. For the 30 ppi RVC, the current efficiency and removal efficiency values found were, respectively, 45 % and 96 % for a solution containing 10 mg L^{-1} of Cd^{2+} ion after 30 minutes electrolysis at –0.90 V while 33 % and 99% were found for the 60 ppi RVC. The concentration decay of Cd^{2+} ion in the solution was monitored after each experiment by anodic stripping voltammetry at a hanging mercury drop electrode.

Keywords: cadmium removal, reticulated vitreous carbon, electrodeposition

Introduction

Heavy metal contamination constitutes one of the major environment concerns since these metals are non-biodegradable and, once released into the environment, they can only be diluted or transformed, not destroyed. As Cd^{2+} ion is one of the most toxic species for animals and human beings, the legal limitations concerning its discharge in effluents are very stringent. The maximum allowed cadmium concentration in effluents is 0.5 mg L^{-1} in Germany, 0.3 mg L^{-1} in the United States and 0.1 mg L^{-1} in Switzerland. These concentration values are only slightly higher than those accepted for mercury,[1] so that quantitative investigation on efficient and low cost processes for wastewater treatment continues to be an area of great interest.

Boyanov *et al.*[2] reported the removal of cadmium from dilute solutions in the concentration range of 100 mg L^{-1} to 5 mg L^{-1} after 7 h electrolysis while Kreysa and Reynvaan,[3] by using an electrochemical reactor with a specific flow rate, observed a concentration decay from 22 to 0.61 mg L^{-1} in the Cd^{2+} ion concentration.

The interest in continuous electrolysis to remove metals from aqueous media by using porous electrodes combined with flowing solutions has been growing recently,[4-5] various geometric shapes and materials being employed to obtain high conversion rates. Among these, carbonaceous materials such as graphite, carbon paste, glassy carbon and reticulated vitreous carbon have been used as working electrodes.[6]

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Reticulated vitreous carbon is a form of glass-like carbon combining some properties of both glass and normal industrial carbon.[7,8] It is a very inexpensive open pore material, with a foam structure and it is available in several porosity grades, from 10 to 100 pores per inch (ppi). It can be easily machined into various geometric shapes, has a high surface area, up to 66 cm^2 cm^{-3} for the 100 ppi standard,[5] and seems to be well suited as an electrode material for flow-through cells.[9,10]

Dutra, Espínola and Borges[10] developed a laboratory scale electrolytic flow-by cell with a RVC cathode, which permitted the purification of deaerated aqueous solutions containing cadmium. Under these conditions, the cadmium concentration dropped from 210 to 0.1 ppm in 85 minutes. In this connection, novel forms of carbon materials, as nanofibers and nanofibers on graphite felt, have been used to remove heavy metals from aqueous effluents streams. With these materials, for an inlet cadmium ion concentration of 100 ppb, removal efficiencies near to 90% were obtained.[6]

The aim of this study is to investigate the removal of Cd^{2+} ion from aerated aqueous solutions containing 5 and 10 mg L^{-1} through reduction at a reticulated vitreous carbon electrode. The experimental conditions simulate the composition of an effluent from which the Cd^{2+} and other ionic species have already been removed by a bulk procedure however still containing an environmentally unacceptable residual concentration of the metallic ion.

Experimental

The electrochemical cell used in this study was a conventional three-electrode assembly, the working electrode being a RVC prism of 1.0 cm x 1.0 cm x 1.5 cm, approximately. RVC electrodes (from Electrosynthesis) with 30, 60 and 100 ppi were fixed to a graphite rod with conducting graphite paint from Ladd Research Industries, Inc., Burlington, Vermont. The auxiliary electrode was a Pt gauze and the reference one was a saturated calomel electrode, SCE, to which all potentials are referred.

A vitreous carbon disc working electrode 5 mm in diameter and a hanging mercury drop electrode were employed, respectively, in the preliminary linear voltammetric experiments and in monitoring the Cd^{+2} ion concentration decay, using a Pt wire as auxiliary electrode.

A 1000 mg L^{-1} cadmium sulfate stock solution was prepared in 5.10^{-3} mol L^{-1} H_2SO_4 from the Merck p.a. reagent previously dried at 110 ± 1 °C for 6 h. The measured pH of the solutions containing 5 and 10 mg L^{-1} of Cd^{2+} ion, prepared by dilution in 0.1 mol L^{-1} K_2SO_4 was 4.8. Reduction of the Cd^{2+} ion in these solutions was carried on onto the RVC electrode at the applied potentials of –0.80, –0.90, –1.10 and –1.50 V, for 30 min, in the presence of dissolved O_2 and under stirring.

The concentration decay of the Cd^{2+} ion in the solutions was followed by anodic stripping voltammetry at a hanging mercury drop electrode[11] using a model 303A polarograph from EGG.

After deposition of the Cd^{2+} ion at the RVC electrode, 200 μL of the sample solution were transferred to another cell containing 10 mL of KCl 0.1 mol L^{-1}, the pH of which was previously adjusted to 4.8 with sulfuric acid. The solution was deaerated with high purity grade N_2 for, respectively, 10 and 4 min, before and after addition of the sample to the supporting electrolyte.

The pre-concentration of cadmium at the hanging mercury drop electrode was carried out at –1.00 V for 30 s. Cadmium was then stripped from the Hg electrode by scanning the potential from –1.00 V to –0.30 V and the peak current, previously calibrated, was employed to determinate the Cd^{2+} ion concentration in the sample solution.

Linear voltammetric experiments at a glassy carbon disc electrode and electrolysis of Cd^{2+} ion solutions at the RVC electrode were carried out with a model DEA 332 potentiostat from Radiometer. All solutions were prepared from analytical grade reagents with bidistilled and deionized water.

Before and after the Cd^{2+} ion electroreduction procedure, the RVC electrode was analyzed by Scanning Electron Microscopy (SEM) using the backscattered electron image (BEI) technique and by Energy Dispersive Spectrometry (EDS). The SEM instrument was a PHILIPS XL30 coupled to an Energy Dispersive Spectrometer (EDS) from Edax. In this technique, a semiconductor detector classifies X-radiation according to its energy rather than its wavelength. All spectra were collected within 100 s using the selected area mode and a 10 mm work distance.

Results and Discussion

Preliminary experiments on the Cd^{2+} ion electroreduction were carried on at sulfuric-sulfate (K_2SO_4 0.1 mol L^{-1} and pH 4.8) aerated solutions containing 10 mg L^{-1} of the metallic ion. The voltammograms in Figure 1 were obtained by linear potential scan voltammetry at 0.02 V s^{-1}, from Esa = 0.00 V to Esc = –1.80 V, using a glassy carbon totating disc electrode (5 mm in diameter) at several angular velocities. It is seen that the Cd deposition begins at –0.90 V, which is in accordance with thermodynamic data[12] for the 4.8 experimental pH employed in this work. A plot of the inverse of the limiting current density (j_{lim}^{-1}) value at –1.00 V against $\omega^{-1/2}$, ω being the angular speed

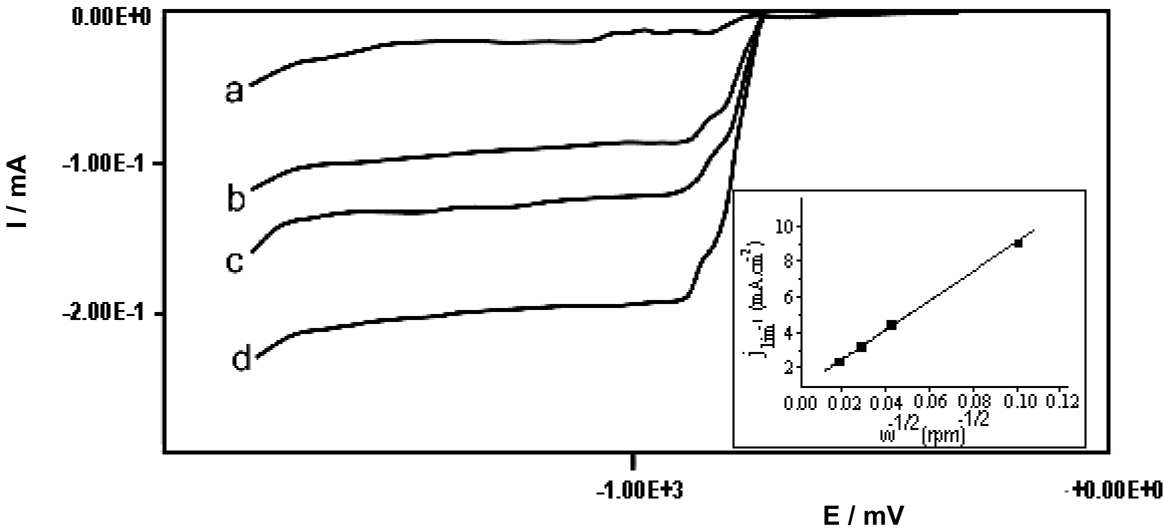

Figure 1. Linear voltammetric curves for Cd^{2+} reduction at a glassy carbon rotating disc electrode. Sulfuric-sulfate (K_2SO_4 0.1 mol L^{-1} and pH 4.8) aerated solution containing 10 mg L^{-1} of Cd^{2+} ion. Potential scans from Esa = 0.00 to Esc = -1.80 V at 0.02 V s^{-1} and electrode rotation speed of (a) 100; (b) 1000; (c) 1500 and (d) 2500 rpm. Insert: j_{lim}^{-1} *vs.* $\omega^{-1/2}$.

of the electrode, shows a straight line that intersects the origin (see insert in Figure 1). This behavior evidences that the cadmium electroreduction is a mass transport controlled reaction in the potential range between –0.90 to –1.10 V in agreement with Levich's equation:[13]

$$j_{lim} = 0.62\, nFD^{2/3}C_o^{*}\omega^{1/2}\nu^{-1/6} \qquad (1)$$

where F is the Faraday constant, n the number of electrons, C_o^{*} is the bulk Cd^{+2} ion concentration, D the diffusion coefficient and ν the kinematic viscosity. Taking a value of 1.17 x 10^{-6} m^2 s^{-1} for the kinematic viscosity of the electrolyte,[14] the diffusion coefficient for Cd^{2+} ion was calculated to be 7.1 x 10^{-10} $m^2 s^{-1}$, which agrees with data in the literature.[15]

The cadmium concentration decay was monitored as a function of time at an applied potential of -1.10 V using RVC 30, 60 and 100 ppi working electrodes and 10 mg L^{-1} Cd^{2+} ion concentration. Figure 2 shows the normalized Cd^{2+} ion concentration as a function of time showing that in sulfuric-sulfate medium at pH 4.8 the Cd^{2+} ion concentration drops exponentially with time, which can be ascribed to a pseudo-first order kinetics reaction. Moreover, an efficiency removal around 99% is detected after 30 min of electroreduction, which means a drop of the Cd^{2+} ion concentration to 0.1 mg L^{-1}.

The efficiency in removing the metallic ion from the solution was evaluated at several applied potentials, using two different concentrations, 5 and 10 mg L^{-1}, in quiescent and stirred solutions. The data in Table 1 were obtained under stirring, after 30 minutes of electrolysis, using a

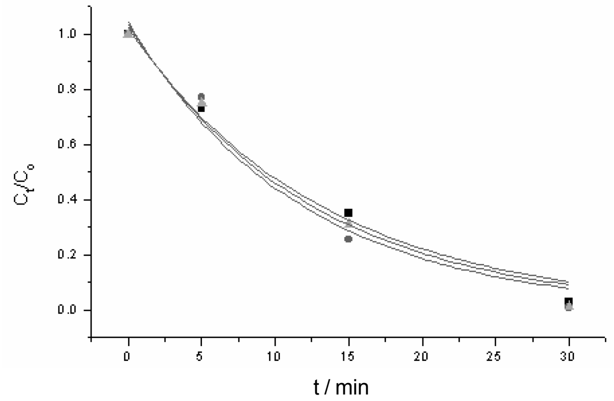

Figure 2. Cadmium concentration decay vs. time for electrodeposition at -1.10 V using 30 (■), 60 (▲) and 100 ppi (●)RVC electrodes. Sulfuric-sulfate (K_2SO_4 0.1 mol L^{-1} and pH 4.8) aerated solution containing 10 mg L^{-1} of Cd^{2+} ion at pH 4.8.

Table 1. Dependence of the cadmium removal efficiency on the applied potential for 30 minutes electrolysis at a 30 ppi RVC electrode. Sulfuric-sulfate (K_2SO_4 0.1 mol L^{-1} and pH 4.8) aerated solutions containing 5 and 10 mg L^{-1} of Cd^{2+} ion

Applied Potential (V)	Removal Efficiency (%) Cd^{2+} initial concentration: 5 mg L^{-1}	Removal Efficiency (%) Cd^{2+} initial concentration: 10 mg L^{-1}
-0.80	42 ± 1	46 ± 1
-0.90	89 ± 1	96 ± 1
-1.10	90 ± 1	97 ± 1
-1.50	90 ± 1	97 ± 1

30 ppi RVC electrode. It is seen that 90% and 97% of the metallic ion are removed, respectively, from the 5 and 10 mg L^{-1} Cd^{2+} ion solutions in the potential range between –0.90 and – 1.10 V. Similar experiments carried out with unstirred solutions showed very low recovery values, around 10% after 90 minutes of electrolysis, thus confirming the dependence of the Cd^{2+} reduction rate on the mass transport regimen.

In a previous work Agarwal *et al.*[5] used a RVC electrode to remove cadmium from dilute aqueous solutions in the pH range of 1.9 to 3.5. A removal efficiency of 92.2% was obtained at –2.75 V for a 25 ppm Cd^{2+} ion solution at pH 2.61 in 0.1 mol L^{-1} supporting electrolyte with a 10 ppi RVC after 11 passes. In the absence of supporting electrolyte the applied voltage increased to –3.00 V and the efficiency dropped to 23 %.

In the present study, the electrodeposition efficiency of a 10 mg L^{-1} Cd^{2+} ion in pH 4.8 medium, was experimentally determined at quite negative potentials using a 30 ppi electrode. Setting the deposition potential at –2.50 V, a 10 % removal efficiency was achieved after 90 minutes of electrolysis, while at –3.00 V the concentration decay was not detectable. This behavior can be explained taking into account that at significantly negative potential values, the rate of the hydrogen evolution reaction plays a determinant role on the overall reaction.[16]

The results in Table 1 show that for less negative potentials, in the range from –0.90 to –1.50 V, higher removal efficiency values are found. On the other hand, the current efficiency of the process was determined for 30 min of electroreduction (Table 2) using RVC electrodes of 30, 60 and 100 ppi at –0.80, –0.90, –1.10 and –1.50 V and an initial Cd^{2+} ion concentration of 10 mg L^{-1}.

Table 2. Dependence of the current efficiency on the applied potential and on the RVC porosity for 30 minutes cadmium electroreduction. Sulfuric-sulfate (K_2SO_4 0.1 mol L^{-1} and pH 4.8) aerated solutions containing 10 mg L^{-1} of Cd^{2+} ion

Applied Potential (V)	Current Efficiency (%) 30 ppi RVC	Current Efficiency (%) 60 ppi RVC	Current Efficiency (%) 100 ppi RVC
-0.80	22 ± 1	25 ± 1	10 ± 1
-0.90	45 ± 1	33 ± 1	18 ± 1
-1.10	38 ± 1	30 ± 1	17 ± 1
-1.50	22 ± 1	24 ± 1	15 ± 1

The theoretical charge needed to reduce 100 % of the 2.50 x 10^{-4} g of Cd^{2+} ion contained in 25 mL of the sample solution is 0.430 C. Since the experimental value obtained for the charge consumed during the Cd^{2+} ion electrodeposition is higher than the theoretical one, the exceeding charge is mostly consumed in the hydrogen evolution and oxygen reduction reactions taking place simultaneously to the Cd^{2+} ion reduction.

Data in Table 2 show that for –1.50 V the current efficiency drops although the Cd^{2+} ion removal efficiency remains unchanged (see Table 1). On the other hand, at –0.80 V both the current efficiency and the removal efficiency (see Table 1) fall probably due to a lower rate of the Cd^{2+} ion reduction reaction.

In the experimental conditions employed in this work, a current efficiency of 33% and removal efficiency close to 99 % were obtained after 30 min of electrolysis at –0.90 V for a 60 ppi RVC electrode and a Cd^{2+} ion concentration of 10 mg L^{-1}. For the same experimental conditions, 96% of the metallic ion was removed when using a 30 ppi RVC electrode and the current efficiency increased to 45%, while the current efficiency dropped to18% when using a 100 ppi RVC electrode.

From these results, it is seen that the recommended potential range to electroreduce Cd^{2+} ion from pH 4.8 aerated sulfuric-sulfate aqueous solutions is comprised between –0.90 and –1.10 V.

Another point, which must be considered, is the current efficiency decrease with increasing RVC porosity that was observed in this optimum potential range. It seems plausible to suppose that this behavior may be related to an increasing amount of hydrogen occluded into the pores of the RVC electrode thus increasing electrical resistance and turning difficult the charge transfer step for cadmium reduction.

Figures 3a and 3b show the SEM and EDS analyses, respectively. The presence of metallic cadmium on the RVC surface after reduction of the Cd^{2+} ion at -1.10 V for 30 minutes can be clearly observed. According to Dutra *et al.*[10] the deposition on preferential sites is due to the non-uniform potential distribution throughout the electrode surface. Additionally, the region of the electrode-electrolyte interface is more densely recovered, due to the Cd^{2+} ion concentration drop throughout the electrode length. The structure of the deposited cadmium seems to be mostly nodular, a characteristic of the mass transfer control mechanism.

Conclusions

It has been shown that Cd^{2+} ion in a concentration level as low as 5 mg L^{-1}, can be electrodeposited onto a RVC electrode from H_2SO_4-K_2SO_4 aerated solutions of pH 4.8. The Cd^{2+} ion reduction is a mass transport-controlled reaction, the metallic ion concentration dropping exponentially with time.

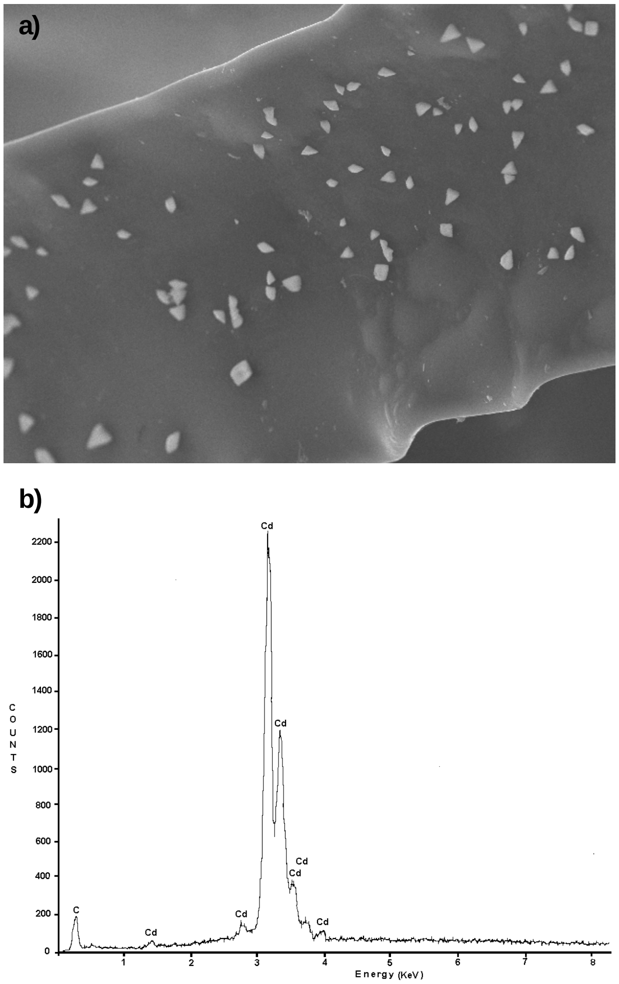

Figure 3. a) SEM analysis of the 60 ppi RVC electrode after Cd electrodeposition at –1.10 V, for 30 minutes. Magnification: 1200 x. b) EDS analysis of the 60 ppi RVC electrode showing the presence of Cd.

The potential range from –0.90 to –1.10 V and the RVC porosity of 30 ppi showed to be the most adequate experimental parameters for cadmium removal in the conditions of this study. The values of current efficiency and removal efficiency achieved at –0.90 V for RVC 30 ppi, were, respectively, 45 % and 96 %, the latter being 3% less than the value found for the 60 ppi porosity. On the other hand, the current efficiency drops with increasing RVC porosity in the same potential range, which is probably related to an increase in the charge consumed in the H_2 evolution and O_2 reduction reactions, occurring simultaneously to the reduction of Cd^{2+}. These results evidence a settelment between the RVC electrode porosity and the Cd^{+2} ion removal efficiency, since a higher electrode surface did not favored the metal reduction rate.

The proposed procedure presents practical interest in the development of flow systems for cadmium removal from effluents where it is present in low concentration levels.

Acknowledgments

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References

1. Bisang, J.M.; Grau J.M.; *J. Chem. Technol. Biotechnol*. **1998**, *73*, 398.
2. Boyanov, B.S.; Donaldson, J.D.; Grimes S.M.; *J. Chem. Technol. Biotechnol.* **1988**, *41*, 317.
3. Kreysa, G.; Reynvaan, C.; *J. Appl. Electrochem*. **1982**, *12*, 241.
4. Pletcher, D.; Whyte, I.; Walsh, F.C.;Millington, J.P.; *J. Appl. Electrochem*. **1991**, *21*, 659.
5. Agarval, I.C.; Rochon, A.M.; Gesser, H.D.; Sparling, A.B.; *Water Res.* **1984**, *18*, 227.
6. Brennsteiner, A.; Zondlo, J.W.; Stiller, A.H.; Stansberry, P.G.; Tian, D.; Xu, Y.; *Energy Fuels* **1997**, *11*, 348.
7. Cowlard, F.C.; Lewis, J.C.; *J. Mater. Sci.* **1967**, *2*, 507.
8. Botelho, E.C.; Scherbakoff, N.; Rezende, M.C.; *Mater. Res.* **2000**, *3*, 19.
9. Wang, J.; Blaedel, W.J.; *Anal.Chem.* **1979**, *51*, 799.
10. Dutra, A.J.B.; Espínola, A.; Borges, P.P.; *Minerals Eng.* **2001**, *13*, 1139.
11. Bard, A.J.; Faulkner, L.R.; *Electrochemical Methods*, J. Wiley & Sons: New YorK, 1980, p.413.
12. Pourbaix, M.; *Atlas d'Équilibre Électrochimiques*, Gauthier-Villars & Cie.: Paris, 1963, p. 406.
13. Bard, A.J.; Faulkner, L.R.; *Electrochemical Methods*, J. Wiley & Sons: New YorK, 1980, p.291.
14. Pletcher, D.; Whyte, I.; Walsh, F.C.; Millington, J.P.; *J. Appl. Electrochem*. **1991**, *21*, 667.
15. Oldham, H.B.; Myland, J.C.; *Fundamentals of Electrochemical Science*; Academic Press: San Diego, 1994, p.233.
16. Vetter, K.J.; *Electrochemical Kinetics*, Academic Press Inc.: London, 1967, p.516.

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