Electroactive Surface Area Evaluation of Platinum Electrodes: A Comparative Study of Voltammetric Methods

Carem E. S. Pereira (G)[1]*; Vitoria B. Messias (PG)[2]; Regina M. Takeuchi (PQ)[1,2]; André L. Santos (PQ)[1,2]

[1] Federal University of Uberlândia, Institute of Exact and Natural Sciences of Pontal,
[2] Federal University of Uberlândia, Institute of Chemistry.
*e-mail: heysouza.carem@gmail.com

RESUMO

A área eletroativa (ECSA) e o fator de rugosidade (RF) permitem a avaliação do desempenho eletrocatalítico de materiais. No entanto, a determinação da ECSA por voltametria cíclica ainda é um tema controverso na literatura. Este estudo compara a ECSA de um eletrodo de Pt (com área geométrica de 0,0707 cm²) obtida por três métodos: (i) capacitância da dupla camada (C_{DL}), (ii) picos de adsorção de hidrogênio e (iii) equação de Randles–Ševčík utilizando sonda redox. Os resultados mostraram que os métodos baseados em C_{DL} e nos picos de hidrogênio forneceram valores de ECSA mais elevados e estatisticamente equivalentes, quando utilizados parâmetros instrumentais adequados. Por outro lado, a equação de Randles–Ševčík resultou em um valor próximo à área geométrica, evidenciando limitações relacionadas à difusão da sonda. A comparação ressalta as vantagens e limitações de cada abordagem, enfatizando a importância da escolha do método mais adequado para cada sistema.

Palavras-chave: área eletroativa, voltametria cíclica, capacitância de dupla camada, adsorção de hidrogênio, equação de Randles–Ševčík.

Introduction

The electroactive surface area (ECSA) and roughness factor (FR) are key parameters for studying electrocatalytic processes and sensor performance. Among the methods used to estimate ECSA, three cyclic voltammetry-based approaches stand out: the determination of double-layer capacitance (C_{DL}), the quantification of charge related to hydrogen adsorption (Q_H), and the application of the Randles–Ševčík (RS) equation. However, ECSA determination via cyclic voltammetry remains a subject of debate in the literature due to methodological variations and the inherent limitations of each approach [1,2,3].

Experimental

All experiments were conducted using a Pt working electrode with a geometric area of 0.0707 cm².

Determination of Double-Layer Capacitance.

The working electrode (WE) was polished with diamond paste (0.25 µm), immersed in HNO_3 1:1 (v/v), and subjected to an ultrasonic bath in an EtOH:H_2O mixture (1:1 v/v), with rinsing using ultrapure water between each step.

Hydrogen Adsorption Peaks

The WE were polished with alumina suspension (0.5 µm) and electrochemically activated through successive cyclic voltammetry scans at different scan rates in H_2SO_4 0,5 mol L^{-1}.

Randles–Ševčík Equation

The electrode was polished with diamond paste (0.25 µm), immersed in HNO_3 1:1 (v/v), and sonicated, with rinsing using ultrapure water between each step. After that, electrochemical conditioning was performed in KCl 0.5 mol L^{-1}. $[Ru(NH_3)_6]^{3+/2+}$ was used as the redox probe in these studies and its diffusion coefficient in KCl 0.5 mol L^{-1} was assumed to be 5.47 x 10^{-6} cm^2 s^{-1} [4].

Results and Discussion

Figure 1 shows the results obtained for each methodology used to determine the ECSA. In (A), the typical capacitive response in regions without faradaic processes for C_{DL} calculation is observed; in (B), the characteristic hydrogen adsorption/desorption peaks in acidic medium; and in (C), the linear relationship between the cathodic peak current (i_{pc}) and the square root of the scan rate ($v^{1/2}$) from cyclic voltammograms recorded in the presence of 5.0 mmol L^{-1} $[Ru(NH_3)_6]^{3+/2+}$ with 0.5 mol L^{-1} KCl.

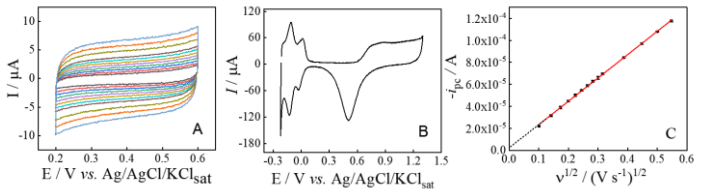

Figure 1. A) Cyclic voltammograms recorded in 0.1 mol L^{-1} KCl with α = 0.3 and ΔEs = 2 mV at various scan rates: (—) 0,3; (—) 0,4; (—) 0,5; (—) 0,6; (—) 0,7; (—) 0,8; (—) 0,9 e (—) 1,0; (—) 1,25; (—) 1,5; and (—) 1,75 Vs^{-1}. B) Cyclic voltammogram recorded in 0.5 mol L^{-1} H_2SO_4 at 500 mV s^{-1} with α = 0.5 and ΔEs = 2 mV. C) Plot of -i_{pc} vs. $v^{1/2}$ constructed from cyclic voltammograms recorded in 0.5 mol L^{-1} KCl containing 5.0 mmol L^{-1} $[Ru(NH_3)_6]^{3+}$ at different scan rates (10 to 300 mV s^{-1}), with α = 1.0 and ΔEs = 2.0 mV.

Each method exhibits distinct profiles, reflecting the different mechanisms involved in estimating the electrode's surface area. For the determination of the area using the Randles–Ševčík equation, a ΔE_p value of 64 mV was obtained, which is consistent with a reversible process; therefore, the equation can be reliably employed to estimate the electrode area. In contrast, achieving these results for the C_{DL}, and hydrogen peak-based methods required careful optimization of instrumental parameters, such as the sampling parameter (α), which defines the timing of current recording during sampling, and the potential step (ΔE_S), which determines the number of data points collected. Table 1 shows the area and RF values obtained for each method under optimized conditions.

Table 1. Electrode area values for Pt determined by different methods.

Method	Main Experimental Parameters	Area / cm²	RF
C_{DL}	α = 0,5 ΔE_s = 2 mV	0,160 ± 0,005	2,26 ± 0,08
Hydrogen Adsorption	α = 0,5 ΔE_s = 2 mV ν = 500 mV s^{-1}	0,173 ± 0,004	2,45 ± 0,05
$[Ru(NH_3)_6]^{3+}$	α = 1,0 ΔE_s = 2 mV	0,0694 ± 0,0006	0,98 ± 0,01

The area determined by the Randles-Ševčík equation is statistically equivalent to the geometric area of the electrode, which indicates that this methodology is inadequate to assess ECSA. At typical timescales of cyclic voltammetry, the diffusion layer reaches approximately 100 µm in thickness. [3,5] Since it extends far beyond the electrode surface, small-scale irregularities may not directly influence current measurements. Therefore, the measured current will be limited by the flux of electroactive species crossing the plane at the outer boundary of the diffusion layer. Thus, the area derived from the Randles–Ševčík equation correspond to the "projected area" which reflects the geometric surface rather than the true ECSA.[3,5] In contrast, the methods based on double-layer capacitance (C_{DL}) and hydrogen adsorption charge (Q_H) yielded RF values consistent with those reported in the literature for polished electrodes ranging from 2 to 3[6]. Moreover, when using optimized instrumental conditions, C_{DL} and Q_H methods provided statistically equivalent ECSA values, with comparable precision, as confirmed by t-test and F-test analyses.

Conclusions

Determining the WE area by cyclic voltammetry is challenging due to various methods of yielding different areas, such as geometric or electroactive. This study showed that the Randles-Ševčík equation estimates the geometric area, not the electroactive one. The C_{DL} and hydrogen adsorption charge methods provided more accurate ECSA values but were strongly influenced by instrumental parameters like sampling rate (α) and potential increment (ΔE_S). Optimal parameters (α = 0.5 and ΔE_s = 2 mV) yielded statistically equivalent results for both methods. Careful optimization and clear reporting of these parameters are crucial for reproducibility and comparability of results.

Acknowledgments

FAPEMIG

References

[1] D. M. Morales; M. Risch, Seven steps to reliable cyclic voltammetry measurements for the determination of double layer capacitance. *J. Phys. Energy*, **2021**.

[2] D. Coelho; G. M. Luiz; S. A. S. Machado, Estimating the Electrochemically Active Area: Revisiting a Basic Concept in Electrochemistry. *J. Braz. Chem. Soc.*, **2021**, 32, 1912–1917.

[3] T. Paixão, Measuring Electrochemical Surface Area of Nanomaterials versus the Randles–Ševčík Equation. *ChemElectroChem*, **2020**, 7, 3414–3415.

[4] Y. Wang; J. G. Limon-Petersen; R. G. Compton, Measurement of the diffusion coefficients of $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{2+}$ in aqueous solution using microelectrode double potential step chronoamperometry. *J. Electroanal. Chem.*, **2011**, 652, 13–17.

[5] V. B. Messias; D. C. P. Modenez; C. E. S. Pereira; R. M. Takeuchi; A. L. Santos, Practical Considerations for Using Redox Probes in Electrochemical Sensor Characterization. *Electrochim. Acta*, **2025**, 511.

[6] A. J. Bard; L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2ª ed., John Wiley & Sons, New York, **2001.**