

Electrochemical Activities of Glassy Carbons Produced by Thermal Degradation of Polyfurfuryl Alcohol Resin

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A manufatura de carbono vítreo através da degradação térmica de uma resina de álcool polifurfurílico a 1000°C e 2000°C sob atmosfera de nitrogênio é descrita e suas atividades eletroquímicas como materiais eletródicos foram investigadas utilizando o sistema redox ferricianeto/ferrocianeto e as técnicas de voltametria cíclica e eletrodo de disco rotatório.

The manufacture of glassy carbon by thermal degradation of polyfurfuryl alcohol resin at 1000°C and 2000°C under nitrogen atmosphere is described and its electrochemical activities as electrode materials have been investigated in terms of the heterogeneous electron transfer reversibility using the ferricyanide/ferrocyanide redox couple as a probe reaction and cyclic voltammetry and rotating disk electrode techniques.

Key words: *glassy carbon.*

Introduction

Glassy carbon, also often referred to as vitreous carbon, has served as the electrode material for numerous studies¹⁻³ because it has the widest potential range compared to many carbon electrodes and other solid electrodes and it is impermeable to gases, highly resistant to chemical attack and electrically conductive. Furthermore, glassy carbon can be used either as the electrocatalyst itself or as a conductive support for an electrochemically active material.

Glassy carbon materials are produced by thermal decomposition of polymeric compounds such as resins of furfuryl alcohol, phenol formaldehyde, acetone-furfural, or furfural alcohol-phenol copolymer and its physical properties are dependent on the maximum temperature of heat treatment¹.

The widespread use of glassy carbon in electrodes, associated with the increasing number of analytical chemists and electrochemists in Brazil and with the difficulty of purchasing such important electrode material in our country, motivated this work to provide a reference source for researchers interested in this area.

In this work, we describe the manufacture of glassy carbons by thermal degradation of polyfurfuryl alcohol resin at two different temperatures (1000°C and 2000°C) under nitrogen atmosphere and its electrochemical activities as electrode material. The electrode activities have been satisfactorily assessed in terms of the heterogeneous electron transfer reversibility using the ferricyanide/ferrocyanide redox couple as a probe reaction and also by comparison with the response of a commercially available glassy carbon electrode and kinetic data reported in the literature.

Experimental

Glassy Carbon Preparation – A resin of furfuryl alcohol with density of 1.25 g/cm³, intrinsic viscosity of 0.023 dl/g, Brookfield viscosity of 3800 cPoise, pH 6.5 at 25°C and ash content of 2500 ppm was obtained by acid catalysis of furfuryl alcohol. The resin was poured into cylindrical recipients and polymerization was done at room temperature, using organic acid as catalyst. After a hardness of 20 units in the Barber Colman scale has been reached, the samples were removed out from the recipients and machined into small cylindrical pieces ($\phi \sim 0.7$ cm and $h \sim 1.0$ cm).

The cylindrical pieces were heated up to 1000° under N₂ atmosphere in a standard furnace with a heating rate of $\sim 10^\circ\text{C}/\text{h}$ to produce the glassy carbon materials designated as GC-1000 ($\phi \sim 0.54$ cm and $h \sim 0.81$ cm). Part of these pieces were further heated up to 2000°C under N₂ atmosphere in a tubular graphite furnace with a heating rate of $300^\circ\text{C}/\text{h}$ to produce the GC-2000 materials ($\phi \sim 0.51$ cm and $h \sim 0.80$ cm).

Electrochemical Measurements – Cyclic voltammetry and rotating disk experiments were conducted with the GC-1000 and GC-2000 glassy carbon disks molded in D.E.R. 324 epoxy resin (Reforplas S.A., São Paulo, SP, Brazil). Similar experiments were also conducted with a commercial rotating glassy carbon disk electrode (GC-P) purchased from Pine Instruments Co. (Grove City, PA, USA).

The cyclic voltammetry and rotating disk electrode polarization measurements were performed with a Pine RDE4 potentiostat coupled with a Hewlett-Packard Mo-

del 7046B X-Y recorder (Palo Alto, CA, USA) and the electrode attached to a Pine ASR analytical rotator.

A three compartment conventional electrochemical cell was used. A platinum ($A \sim 2 \text{ cm}^2$) and a saturated calomel electrode (SCE) served as the counter and reference electrodes, respectively. All potentials in the present work are referred to this reference electrode. The final polishing for the disk electrodes was performed with $0.05 \mu\text{m}$ alumina suspended in water. It was then washed with water and electrolyte under ultrasonic agitation, rinsed with water and immediately introduced into the electrochemical cell. All solutions were prepared with reagent grade chemicals and water purified by distillation and purification in a "Milli-Q" system (Millipore Ind. Com. Ltda., São Paulo, SP, Brazil). All experiments were performed with the solutions saturated with "super dry" nitrogen (S.A. White Martins, São Paulo, SP, Brazil).

Results and Discussion

Figure 1 shows the cyclic voltammetry curves of the GC-1000, GC-2000 and GC-P electrodes in deaerated $0.05 \text{ M H}_2\text{SO}_4$ solutions. The tilt of the voltammetry curves are probably due to either solution filled microstructure in the glassy carbon surfaces or slight penetration of electrolytic solution between the side of the GC disks and the seals. Taking into account the electrode active areas, the former explanation is more likely since the electrochemical response of the GC-1000 electrode is more tilted and indicates a much higher apparent double layer capacitance when compared to the GC-2000 response. Nevertheless, all the electrodes presented a similar behavior with a not well defined redox process at approximately 0.25 V (Fig. 1), which it is believed to be associated with the oxidation and reduction of surface oxide groups on carbon and graphite materials^{1,4,5}.

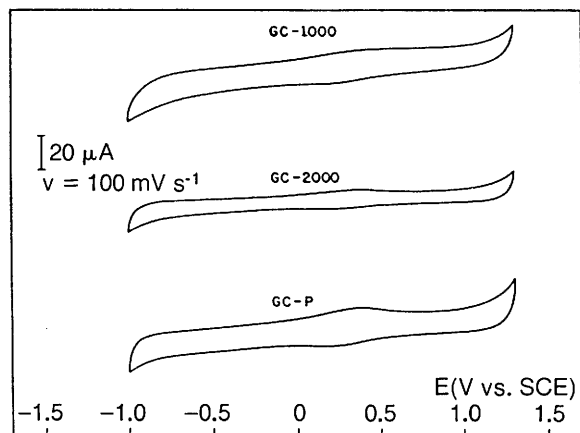


Figure 1. Cyclic voltammograms of glassy carbon electrodes in N_2 saturated $0.05 \text{ M H}_2\text{SO}_4$ solution at room T . Electrode areas: 0.24 , 0.21 and 0.41 cm^2 for the GC-1000, GC-2000 and GC-P electrodes, respectively.

The potential working range of the GC electrodes in aqueous solutions is illustrated in Fig. 2 with the cyclic voltammograms of the GC-2000 electrode. A wide potential range, extending over spans of 2.5 V in aqueous solutions (depending on pH) is available and compares favorably with those reported in the literature¹.

In order to examine the electrochemical activities of the GC-1000 and GC-2000 glassy carbon materials produced by thermal degradation of polyfurfuryl alcohol re-

sin, the ferrocyanide/ferricyanide redox couple was utilized as a probe reaction. This redox system has been extensively studied⁶⁻²⁶ and it was chosen because the electron transfer rate has been shown to be very sensitive to the state of the glassy carbon surface^{10,19,21,23}.

Typical cyclic voltammograms of ferricyanide/ferrocyanide in $0.5 \text{ M K}_2\text{SO}_4$ solution are illustrated in Fig. 3

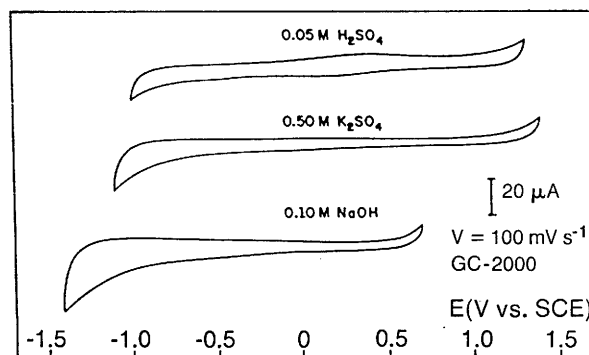


Figure 2. Cyclic voltammograms of GC-2000 electrode in N_2 saturated aqueous media at room T . Electrode area: 0.21 cm^2 .

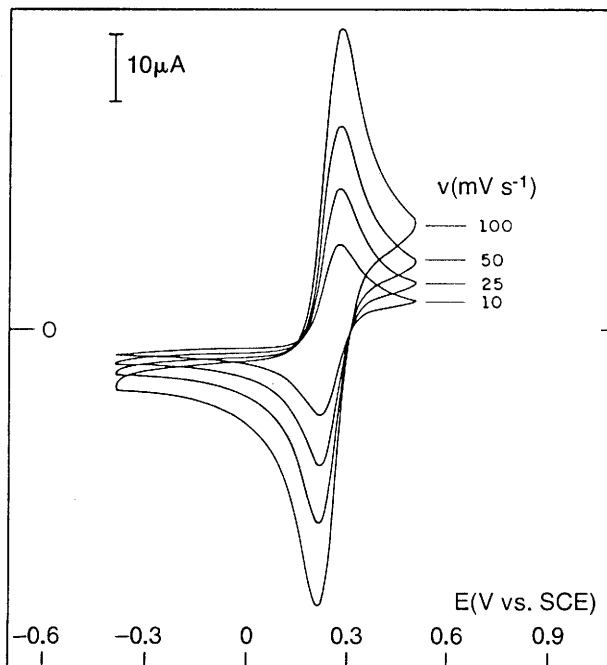


Figure 3. Cyclic voltammograms at different scan rates of ferricyanide at GC-2000 electrode ($A \sim 0.21 \text{ cm}^2$). Solution conditions: $1.0 \text{ mM K}_3[\text{Fe}(\text{CN})_6]$, $0.5 \text{ M K}_2\text{SO}_4$, N_2 saturated, room T .

for the GC-2000 electrode. The scan rates were varied from 10 to 200 mV/s . The separations between anodic and cathodic peak potentials ($\Delta E_p = E_{pa} - E_{pc}$) were independent of scan rate and were constant at a value of $65 \pm 3 \text{ mV}$. The ratios between the anodic peak and cathodic peak currents ($|I_{pa}/I_{pc}|$) for different scan rates were also constant at a value of 1.05 ± 0.05 . These observations are in agreement with those expected ($\Delta E_p = 59 \text{ mV}$ and $|I_{pa}/I_{pc}| = 1.0$) for a reversible one-electron transfer reaction²⁷⁻²⁹.

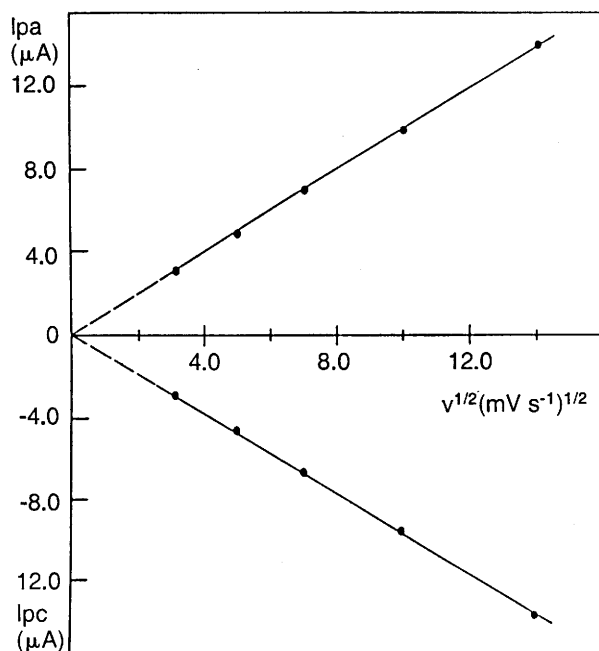


Figure 4. Dependence of the anodic and cathodic current peaks of ferricyanide at GC-2000 electrode with scan rate. Data taken from Figure 3.

For a given voltammetric peak, assuming ideal Nernstian behavior and diffusion control, the peak current (I_p in A) is related to the potential scan rate (v in V/s) by the equation²⁷⁻²⁹:

$$I_p = [(2.69 \times 10^5) n^{3/2} A C_b D^{1/2}] v^{1/2} \quad (1)$$

where n is the number of electrons involved in the reaction, A is the electrode area (cm^2) and C_b and D are the bulk concentration (mol/cm^3) and the diffusion coefficient (cm^2/s), respectively, of the electroactive species in solution. Therefore, a plot of I_p vs $v^{1/2}$ should be linear and pass through the origin. Figure 4 shows such a plot and the linearity provides evidence that Eq. 1 is applicable. From the value of the slope and using Eq. 1 with $n = 1$ and $C_b = 1.0 \times 10^{-6} \text{ mol}/\text{cm}^3$, the relation between A and D resulted to be $AD^{1/2} = 5.803 \times 10^{-4} \text{ cm}^{5/3}/\text{s}^{2/3}$. To evaluate the electrode area and the diffusion coefficient values without any assumptions, rotating disk electrode experiments were also performed.

Rotating disk polarization curves obtained with the GC-2000 electrode in $0.5 \text{ M K}_2\text{SO}_4$ solution containing $1 \times 10^{-3} \text{ M K}_3[\text{Fe}(\text{CN})_6]$ are shown in Fig. 5. For potentials less positive than 0.1 V , the current is entirely limited by mass transport. The equation relating the limiting current (I_L in A) and the electrode rotation rate (ω in rad/s or f in rpm), at a given potential, is the Levich equation^{28,29}:

$$I_L = \left[\frac{0.20 n F A D^{2/3} C_b \nu^{-1/6}}{0.62 n F A D^{2/3} C_b \nu^{-1/6}} \right] \omega^{1/2} \quad (2)$$

where ν is the kinematic viscosity of the electrolyte (cm^2/s) and F is the Faraday constant. Therefore, a plot of I vs $f^{1/2}$ should be linear with zero intercept, as shown in Fig. 6. From the slope of such a plot and using³⁰ Eq. 2 with $\nu = 9.79 \times 10^{-3} \text{ cm}^2/\text{s}$, and the values of n and C_b as in Eq. 1, it was found that $AD^{2/3} = 8.085 \times 10^{-5} \text{ cm}^{8/3}/\text{s}^{2/3}$. By combining this data with that obtained before with cy-

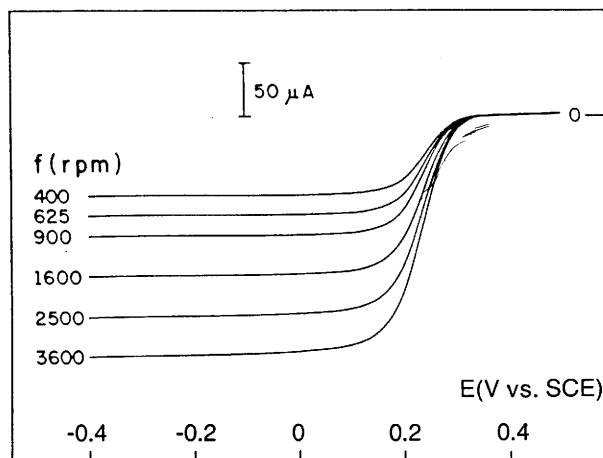


Figure 5. Rotating disk polarization curves at 10 mV s^{-1} for ferricyanide reduction on GC-2000 electrode. Solution conditions as given in Figure 3.

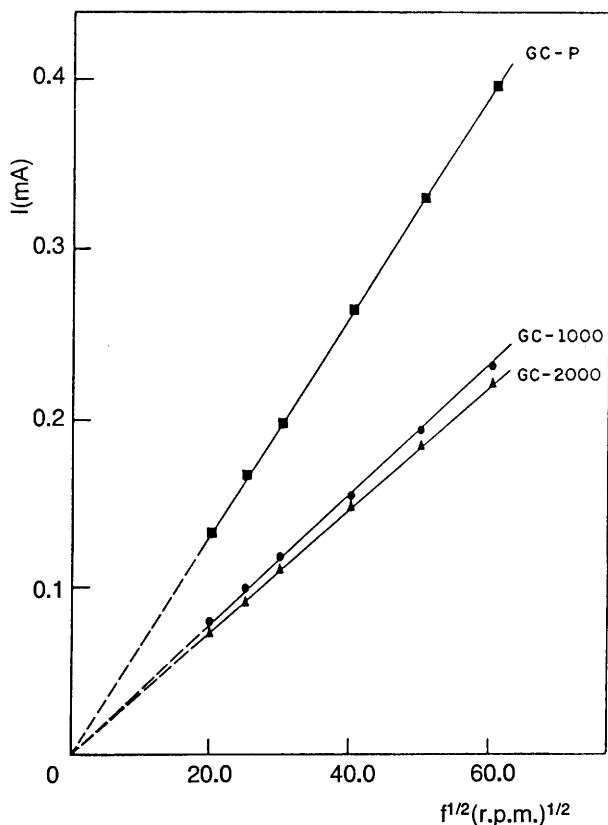
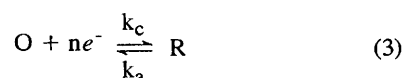


Figure 6. Levich plots for ferricyanide reduction on GC-1000, GC-2000 and GC-P electrodes. Solution conditions as given in Figure 3.

lic voltammetry, the values of the diffusion coefficient and the GC-2000 electrode area resulted to be $7.31 \times 10^{-6} \text{ cm}^2/\text{s}$ and 0.21 cm^2 , respectively.

The diffusion coefficient value obtained agrees well with the $7.63 \times 10^{-6} \text{ cm}^2/\text{s}$ quoted in Refs. 31 and 32. Rotating disk experiments were also performed with the GC-1000 and GC-P electrodes (see Fig. 6) and the calculated areas were 0.24 cm^2 and 0.41 cm^2 , respectively.

For an electrode reaction



the rate constants for the cathodic (k_c) and for the anodic (k_a) reactions are related to potential (E) as follows^{6,28,29}:

$$k_c = k^0 \exp \left[\frac{-\alpha_c n F (E - E^0)}{RT} \right] \quad (4)$$

and

$$k_a = k^0 \exp \left[\frac{\alpha_a n F (E - E^0)}{RT} \right] \quad (5)$$

where k^0 is the standard heterogeneous rate constant, α_c and α_a are the transfer coefficients for the cathodic and anodic reactions, respectively, E^0 is the formal potential of the redox system, and the other terms have their usual meanings. For a simple electron transfer $\alpha_a + \alpha_c = 1$.

Furthermore, if the reaction given by Eq. 3 is a first-order reaction and it is occurring at the rotating disk electrode under both charge transfer and mass transport control, the observed currents are given by^{6,33}:

$$I = \frac{n F A C_b D}{\delta + \frac{D}{k(E)}} \quad (6)$$

where $\delta = 1.61 D^{1/3} \nu^{1/6} \omega^{-2}$ is the thickness of the diffusion layer and $k(E)$ is the heterogeneous rate constant (k_c or k_a) at a given potential E . For large values of $k(E)$, the term $D/k(E)$ can be dropped to give the familiar Levich equation (Eq. 2), i.e., the limiting current of a diffusion controlled process. On the other hand, for small values of $k(E)$ such the magnitude of δ is negligible with respect to the term $D/k(E)$, the current is entirely controlled by charge transfer (kinetic control) and Eq. 3 becomes:

$$I_k = n k(E) F A C_b \quad (7)$$

Substitution of Eqs. 2 and 7 into Eq. 6 leads to the relation:

$$I_k = \frac{I_L \times I}{I_L - I} \quad (8)$$

Thus, Eq. 7 can be rewritten as

$$\frac{I_L \times I}{I_L - I} = n F k(E) C_b \quad (9)$$

Therefore, at a given rotation rate, values of k (k_a or k_c) can be easily evaluated as a function of potential E from the rotating disk polarization curves. Then, $\ln k_a$ and $\ln k_c$ can be plotted as a function of E and, according to Eqs. 4 and 5, two straight lines with intersection at E^0 , should be obtained. From the slopes of the lines, the values of the transfer coefficients α_a and α_c can be determined and from the intersection, the value of k^0 can be evaluated. Such plots were constructed from the experimental data obtained for the GC-1000 and GC-2000 electrodes (Fig. 7) in 0.5 M K_2SO_4 solution containing 1×10^{-3} M $K_3[Fe(CN)_6]$ (cathodic branch) and 1×10^{-3} M $K_4[Fe(CN)_6]$ (anodic branch) and the resulting kinetic parameters, as well as those of the GC-P electrode under similar conditions, are summarized in Table 1.

The kinetic parameters obtained for the GC-1000 and GC-2000 electrodes compared favourable with those observed on the commercial GC-P electrode and also with the values reported in the literature (see Table 1). The discrepancies among the kinetic parameters can be explained by the fact that the electrochemical performance of carbon surfaces is strongly dependent of the electrode pretreatment and various procedures for enhancing the electrocatalytic activity and selectivity of carbon surfaces have been evaluated^{1,17,19-26}. In addition, cyclic voltammetry is not very sensitive to α values unless very high scan rates are employed³⁴.

In conclusion, the electrochemical activities of the GC-1000 and GC-2000 electrodes resulted to be very satisfactory based on the kinetic parameters obtained for the ferricyanide/ferrocyanide system and comparison with the performance of a commercial glassy carbon electrode. Some indication of higher value of apparent double layer capacitance for the GC-1000 electrode was observed, although the present data do not provide sufficient evidence and more specific experiments are required. Additional electrochemical, scanning electron microscopic and X-ray photoelectron spectroscopic examinations of these electrodes are in progress and will be reported in the near future.

Table 1. Electrode kinetic parameters of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system

Electrode	Supporting Electrolyte	Kinetic parameter				Ref.
		E^0 (V)	k^0 (cm/s)	α_c	α_a	
GC-1000	0.5 M K_2SO_4	0.23	4.6×10^{-3}	0.61	0.53	a
GC-2000	0.5 M K_2SO_4	0.22	3.7×10^{-3}	0.39	0.60	a
GC-P	0.5 M K_2SO_4	0.21	4.7×10^{-3}	0.39	0.44	a
GC-30S	0.1 M Phos ^b	0.25	4.7×10^{-3}	0.23	—	14
GC	0.1 M Phos ^b	—	5.4×10^{-3}	—	0.69	14
			1.4×10^{-3}	0.20	—	13
GC	0.5 M KNO_3	0.22	2.8×10^{-3}	—	0.80	13
			2.2×10^{-3}	—	0.63	20
GC	1.0 M KCl	0.23	7×10^{-2}	—	—	24
GC-20	1.0 M KCl	—	4×10^{-3}	—	—	25
GC-A	0.5 M K_2SO_4	—	2.5×10^{-2}	0.50	—	10
			9.0×10^{-4}	0.35	0.40	10

^aThis work

^bPhos: phosphate buffer at pH 7.5

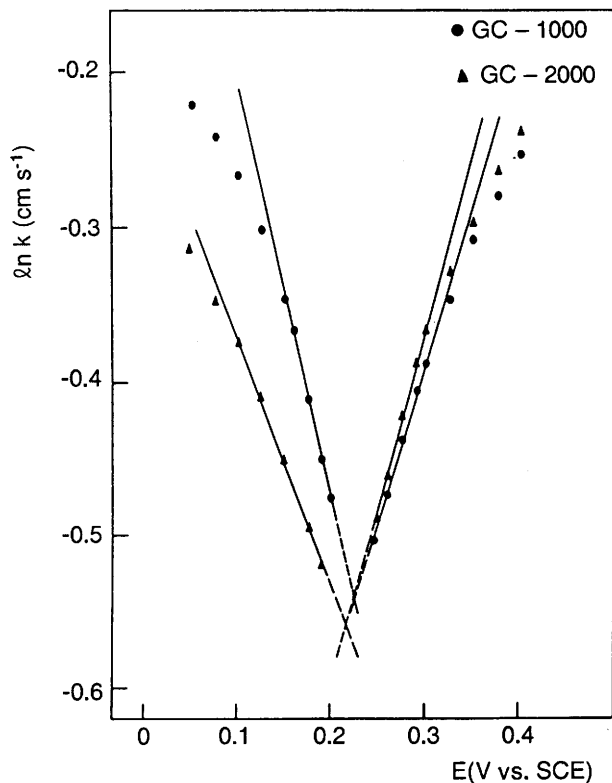


Figure 7. Plots of $\ln k$ as a function of electrode potential for the ferricyanide/ferrocyanide redox couple on GC-1000 and GC-2000 electrodes (see text for details).

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