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To cite this article: L'ubomír Pikna, Mária Heželová & Lenka Šestinová (2017) Application of different types of carbon nanotubes as PIGE surface modifier in Pd(II) electrochemical determination, Particulate Science and Technology, 35:2, 227-232, DOI: 10.1080/02726351.2016.1150372

To link to this article: <http://dx.doi.org/10.1080/02726351.2016.1150372>



Published online: 20 Apr 2016.



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Application of different types of carbon nanotubes as PIGE surface modifier in Pd(II) electrochemical determination

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ABSTRACT

Nowadays, carbon nanotubes with differences in specific surface area, dopants, or functional groups are used in a number of applications, electrolysis not excluding. Various types of carbon nanotubes could improve bare graphite electrode properties by different way and so result in obtaining the different records for the same analyte. The automobile catalysts represent mobile sources of palladium. Levels of palladium in environment are continuously increasing and they need to be monitored. Electrochemistry is a useful and inexpensive component of the field of environment monitoring. For Pd(II) electrochemical determination, six types of carbon nanotubes were used as paraffin impregnated graphite electrode (PIGE) surface modifiers. Voltammetric determination brought interesting results of LOD, LOQ, standard and relative precisions of the method. These parameters as well as prediction intervals were calculated according to the technical procedure DIN 32 645 for the six electrodes and three pH values. Modification of PIGE with nitrogen doped carbon nanotubes (LOD = $1.91 \times 10^{-5} \text{ mol L}^{-1}$ or $3.14 \times 10^{-5} \text{ mol L}^{-1}$ for pH 3 and pH 4.5, respectively) seems very promising. In laboratory, functionalized carbon nanotubes, with specific surface area $200 \text{ m}^2 \text{ g}^{-1}$, provided LOD = $1.49 \times 10^{-5} \text{ mol L}^{-1}$ (pH = 3) and $1.42 \times 10^{-5} \text{ mol L}^{-1}$ (pH = 4.5)

KEYWORDS

Carbon nanotubes; cyclic voltammetry; palladium; paraffin impregnated graphite electrode; solid electrodes

Introduction

Palladium is a steel-white, ductile metallic element resembling and occurring with the other platinum group metals (PGMs) and nickel. It exists in three states: Pd (metallic), Pd(II), and Pd(IV) and can form organometallic compounds, only few of which have found industrial uses. Owing to the ability of palladium ions to form complexes, they bind to aminoacids (e.g., L-cysteine, L-methionine), proteins (e.g., casein, silk fibroin, a lot of enzymes), DNA, or other macromolecules (e.g., vitamin B6). Palladium metal is stable in air and resistant to attack by most reagents except aqua regia and nitric acid. Under appropriate pH and redox potential conditions, it is assumed that peptides or humic or fulvic acids bind palladium in the aquatic environment (Alt et al. 1997). Palladium and its alloys are widely used as catalysts in the petrochemical and, above all, the automotive industries. Concentrations of palladium in surface water, where it is detected, generally range from 0.4 to 22 ng L^{-1} (fresh water) and from 19 to 70 pg L^{-1} (salt water). Concentrations reported in soil range from <0.7 to $47 \text{ } \mu\text{g kg}^{-1}$. The most toxic compound is palladium(II) chloride, and the least toxic compound is palladium(II) oxide. Functional or histological changes in the kidney were found both with palladium compounds and with elemental palladium powder (WHO 2002). The principal uses of palladium are in electronics, industrial catalysts, circuitry, dental alloys, jewelry, and in automobile catalysts (Kielhorn et al. 2002). PGM particles emitted from automobile catalysts deposit on the road surface or in the roadside environment. The soluble fraction of

Pt has been reported to be less than 10% of total amount of Pt in exhaust fumes of gasoline and diesel catalysts, but for Pd and Rh, the soluble fraction was in the same order of magnitude as the particulate fraction. This implies that the effects of Pd and Rh emissions could have a more adverse effect on the environment than Pt emissions (Moldovan et al. 2002). Environmental routes for platinum group elements to biological materials (microorganisms, plants, animals) including sources, transport, transformation as well as bioaccumulation, were reviewed by Ek, Morrison, and Rauch (2004).

Follows from the above, palladium and metals used in catalysts preparation start to pose similar environmental risks that once lead or cadmium. Therefore, environmental monitoring of these metals is necessary and spectral methods as atomic absorption spectrometry with flame or electrothermal atomization, ICP, spectrophotometry, XPS analysis as well as electrochemical methods could be used (Janegitz et al. 2011). Electrochemical methods are in center of interest because of sensitivity, good selectivity, low-cost operation, simple handling, and records interpretation. Different electrochemical methods use differently modified working electrodes (Janegitz et al. 2011; Wang and Jia 2012). Locatelli, Melucci, and Torsi (2005) compared voltammetric and atomic absorption spectrometric determination of PGMs. With regard to precision, accuracy and LOD, comparable results can be obtained with the two techniques, but voltammetry was better than spectroscopy in enabling simultaneous metal determinations and because it did not require addition of matrix modifier.

Table 1. Carbon nanotubes characteristics.

Nanotubes sign	Outer diameter/nm	Length/ μm	SSA ⁺ /m ² g ⁻¹	Functionalization	Producer	Sign of modified PIGE
M-200	40–60	0,5–500	200	–	Sigma-Aldrich	PM200
MC200-D	40–60	0,5–500	200	–COOH lab made ⁺⁺	Sigma-Aldrich	PMC200*
MC200-K	10–20	0,5–2	200	–COOH 2%	TimesNano	PMC200
MC500-K	<8	0,5–2	500	–COOH 3,86%	TimesNano	PMCS500
MN79-K	30–50	10–30	79	N-doped 2,98%	TimesNano	PMN79

⁺Specific surface areas of materials were declared by producers.

⁺⁺Lab made functionalization – carbon nanotubes in a concentrated nitric acid refluxed within 6 h, filtered and washed with distilled water, dried at 105°C to constant weight.

Several papers reporting the voltammetric determination of PGMs in environmental samples were published in the last two decades. Different working electrodes were used for voltammetric determination of PGMs (Hoppstock et al. 1989; Wang and Taha 1991; Messerschmidt et al. 1992; Heinrich, Schmidt, and Kratz 1996; Hoppstock and Michulitz 1997; León et al. 1997; Ye et al. 1998; Locatelli 2005; Locatelli, Melucci, and Torsi 2005; Locatelli 2006). Electrochemical methods have usually been applied to the determination of single element only, prevalently Pt(II) and more rarely Pd (II). The different electrodes as classic HMDE (Locatelli et al. 2005, Locatelli 2006), modified glassy carbon (Ye et al. 1998) or screen-printed electrodes (Silwana et al. 2014) were used for palladium determination.

Present paper deals with modification of another type of solid electrode – PIGE, with different types of carbon nanotubes used as modifiers. Unlike results with single-walled carbon nanotubes (SWCNT), most favorable results were achieved with multi-walled carbon nanotubes MWCNT, what was the reason of their application in this study. The aim was to find the suitable combination PIGE/modifier, which could serve as usable electrochemical sensor of Pd(II) ions.

Material and methods

All of the electrochemical experiments were performed using potentiostat ECA STAT 110 PS (Istran spol. s r.o., BA, Slovakia). A conventional three-electrode system was used with unmodified and modified PIGEs (diameter: 4 mm, electrode area in contact with electrolyte: 12.56 mm²) as the working electrode, a saturated Ag/AgCl (3 mol L⁻¹ KCl) as the reference electrode and a Pt plate (1 cm²) as the counter electrode. A standard solution containing Pd(II) with concentrations of 1 × 10⁻² mol L⁻¹ was prepared from Na₂[PdCl₄] (PdCl₂, NaCl). The method of standard solution addition was used for measurement in Pd(II) concentration range 9.90 × 10⁻⁵ to 2.53 × 10⁻⁴ mol L⁻¹. All of the used reagents were analytically pure, and all of the solutions were prepared with ultrapure water.

Cyclic voltammetry experiments were performed in a potential range from 1.5 to –1.0 V vs. Ag/AgCl. The scan rate was 50 mV s⁻¹. Before each set of measurements, electrochemical cleaning of the electrode was done by measuring of five voltammetric cycles in 0.2 mol L⁻¹ HNO₃. The voltammetric behavior was studied in 0.4 mol L⁻¹ acetate buffer with pH value 3, 4.5, and 7. After measurement, potentiostatic treatment of the electrode was performed at a potential of 700 mV vs. Ag/AgCl for 60 s to dissolve potential traces of Pd undissolved in voltammetric mode.

Electrolytes were deoxygenated using nitrogen gas passing through a solution of pyrogallol. During the measurements, a gentle gas flow was kept above the electrolyte solution.

MWCNT with different specific surface areas and different functionalization (Table 1) were used for modification of PIGEs. PIGEs were modified by drop-casting the CNT suspension onto the prepared surface. A total suspension volume of 40 μl on the electrode surface was added by pipetting sequential 20 μl volumes; after each addition, the sample was left to dry at room temperature. The modification of the PIGEs consisted of the addition of CNT dispersion in nitric acid. Suspension preparation was described in detail in our previous papers (Pikna, Kováčová, and Heželová 2014; Pikna, Heželová, and Kováčová 2015).

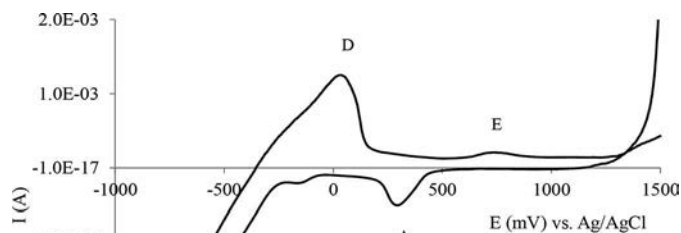


Figure 1. Cyclic voltammogram of Pd(II) (2.53×10^{-4} mol L⁻¹) on PMC200*, acetate buffer pH 4.5.

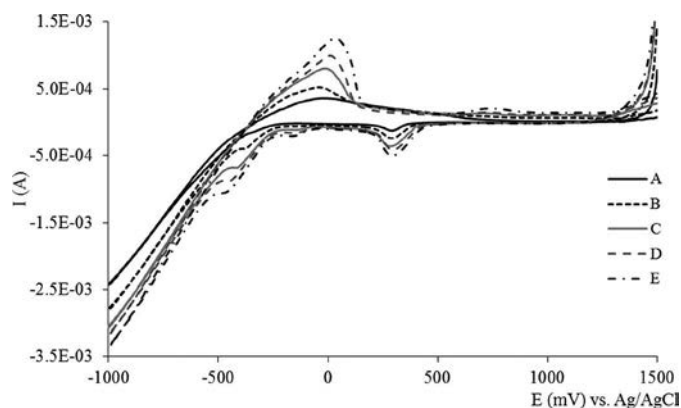


Figure 2. The cyclic voltammograms measured with PMC200* in electrolyte with pH = 4.5 for different concentrations of Pd(II): (A) 9.90×10^{-5} mol L⁻¹ (B) 1.38×10^{-4} mol L⁻¹ (C) 1.77×10^{-4} mol L⁻¹ (D) 2.15×10^{-4} mol L⁻¹, and (E) 2.53×10^{-4} mol L⁻¹.

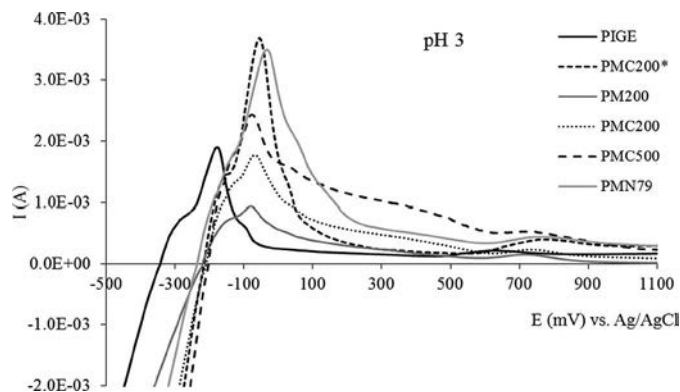


Figure 3. Anodic part of cyclic voltammograms of Pd(II) ($2.53 \times 10^{-4} \text{ mol L}^{-1}$) measured with electrodes PIGE, PMC200*, PM200, PMC200, PMC500, and PMN79 in electrolyte with pH = 3.

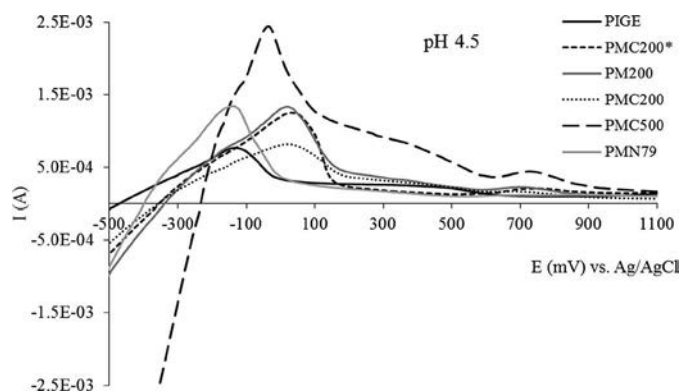


Figure 4. Anodic part of cyclic voltammograms of Pd(II) ($2.53 \times 10^{-4} \text{ mol L}^{-1}$) measured with electrodes PIGE, PMC200*, PM200, PMC200, PMC500, and PMN79 in electrolyte with pH = 4.5.

Results and discussion

In Figure 1, there is a cyclic voltammogram of Pd(II) in acetate buffer measured by PMC200* electrode. Within the scanning potential range of 1.5 to -1.0 V (vs. Ag/AgCl), there are two oxidation peaks and three reduction peaks, all of which associate with palladium. This result is in good agreement to result of Liu et al. (2013) where Pd(II) was measured in nitric acid with platinum electrode. The five marked peaks correspond to reduction of Pd(II) ions from solution (A), adsorption of hydrogen to palladium surface (B), hydrogen reduction (C),

hydrogen desorption from palladium surface (D), and oxidation of Pd(II) to solution (E).

The evaluation of measured voltammetric curves were realized according to anodic peak marked (D), representing hydrogen desorption from palladium surface, because it has been well defined and it was present in all measured curves.

The different types of binders for CNT application onto PIGE surface were tested in our previous work (Pikna, Kováčová, and Heželová 2014). Binders which provided good results in combination with GC electrodes (most widely used electrode for

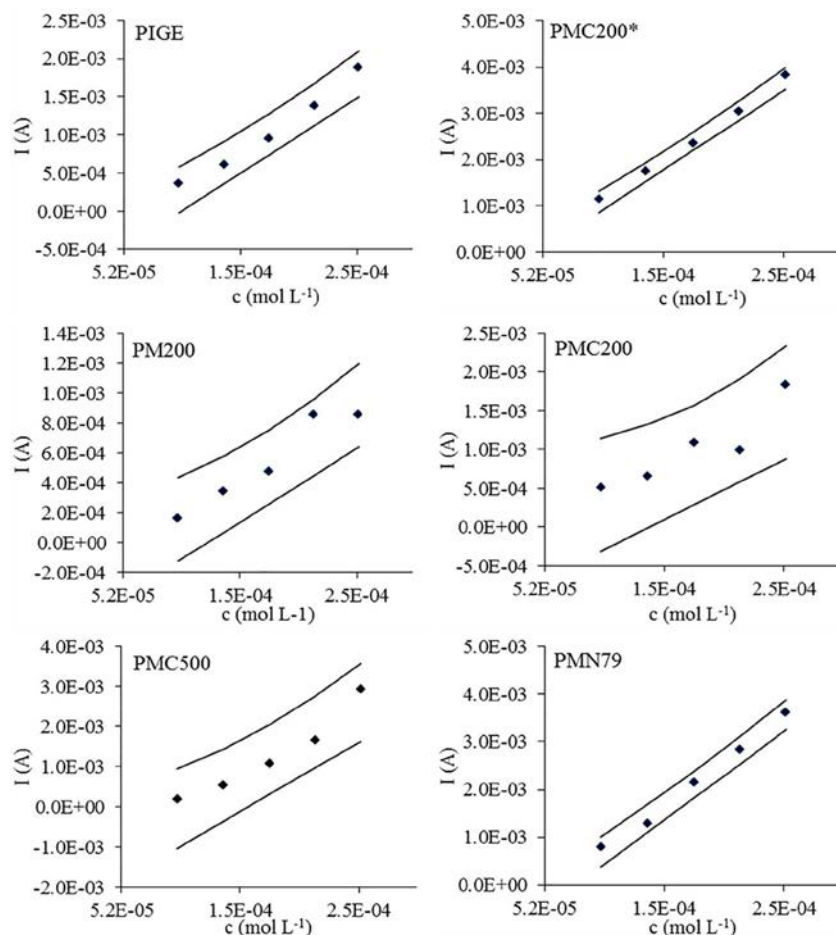


Figure 5. Prediction limit of confidence for Pd(II) measured with electrodes PIGE, PMC200*, PM200, PMC200, PMC500, and PMN79 in electrolyte with pH = 3.

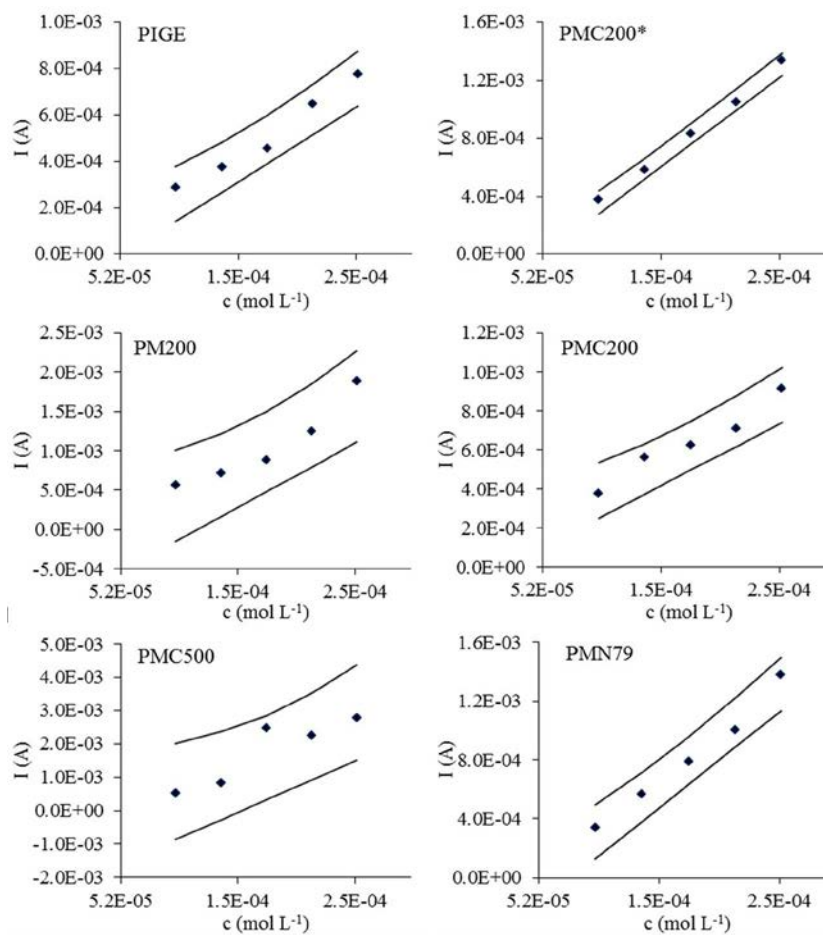


Figure 6. Prediction limit of confidence for Pd(II) measured with electrodes PIGE, PMC200*, PM200, PMC200, PMC500, and PMN79 in electrolyte with pH = 4.5.

modification with CNT) were applied by other authors and were less suitable for PIGE and vice versa. The optimal validation characteristics and highest current response provided PIGE modified with carbon nanotubes dispersed in concentrated nitric acid. Therefore, this binder was used for the aim of current study: preparation of electrodes modified with different types of CNT. It could be expected that CNT's properties will directly influence electrochemical measurements. Acetate buffer was chosen for good pH stability. Cyclic voltammograms for unmodified and modified electrodes were similar to those shown in Figure 1. The increase of current responses after Pd(II) concentration raising (method of standard addition) allowed calibration curves construction (Figure 2).

The anodic parts of the cyclic voltammograms measured in pH = 3 and 4.5 at different electrodes are shown in Figures 3 and 4. Impact of CNT type used for measurement is significant in peak high and peak position. Anodic peak position of hydrogen desorption changed from -34 mV for PM200 and PMC200 to -192 mV for unmodified PIGE in pH = 3 and from 20 mV for PMC200 to -202 mV for PMN79 in pH = 4.5. The pH effect was reflected in peak potential shifting to more positive values, when pH was increased.

Voltammetric records were evaluated and data were used for construction of calibration curves with prediction limits of confidence (Figures 5 and 6). The each point of calibration curve was measured three times. These results showed narrow

Table 2. Validation characteristics for unmodified and modified PIGEs in 0.4 mol L^{-1} acetate buffer with different pH for Pd(II).

pH	Electrode	Limit of detection (LOD) mol L^{-1}	Limit of quantification (LOQ) mol L^{-1}	Standard method precision ($s \times 0$) mol L^{-1}	Relative method precision ($V \times 0$)
3	PIGE	3.46×10^{-5}	7.86×10^{-5}	1.00×10^{-5}	5.68%
	PMC200*	1.49×10^{-5}	4.68×10^{-5}	4.31×10^{-6}	2.44%
	PM200	6.38×10^{-5}	1.14×10^{-4}	1.85×10^{-5}	10.47%
	PMC200	1.06×10^{-4}	3.52×10^{-4}	3.08×10^{-5}	17.43%
	PMC500	6.42×10^{-5}	1.15×10^{-4}	1.86×10^{-5}	10.53%
	PMN79	1.91×10^{-5}	5.62×10^{-5}	5.53×10^{-6}	3.13%
4.5	PIGE	4.12×10^{-5}	8.44×10^{-5}	1.19×10^{-5}	6.75%
	PMC200*	1.42×10^{-5}	4.52×10^{-5}	4.12×10^{-6}	2.33%
	PM200	7.94×10^{-5}	1.70×10^{-4}	2.30×10^{-5}	13.02%
	PMC200	5.01×10^{-5}	9.20×10^{-5}	1.45×10^{-5}	8.22%
	PMC500	1.06×10^{-4}	3.49×10^{-4}	3.06×10^{-5}	17.36%
	PMN79	3.14×10^{-5}	7.53×10^{-5}	9.11×10^{-6}	5.16%

prediction limits of confidence for electrodes PMC200* and PMN79 in both pH. All the others used electrodes had wider or very wide prediction limits of confidence (high variability of measured values). Therefore, they could not be used for serious measurement and Pd(II) determination in the future.

In the CNT-modified sensor preparation process, the current response peak height was only one of the six monitored parameters. Also the other calculated chemometric characteristics were used for describing the quality and/or improvement of bare electrode materials. The LOD, LOQ, standard, and relative precision of the method as a prediction intervals were calculated for six electrodes and two pH values. It is evident from the results in Table 2 that the above-mentioned characteristics varied from case to case. The LOD values ranged from 1.42×10^{-5} to 1.06×10^{-4} mol L⁻¹. Comparison of calculated validation characteristics for unmodified and modified electrodes resulted in better suitability of PMC200* and PMN79 for Pd(II) determination.

Conclusions

Electroanalytical methods applying electrodes modified with carbon nanotubes show different ways of utilization and implementation of nanostructures into devices for improving of routine analyses. These modifications require extensive research for best adaptation into new processes. Present work compared unmodified graphite electrode with different carbon nanotubes modified electrodes. Five types of nanotubes provided five cyclic voltammograms and six results of tested parameters. Measured and calculated results for unmodified and modified electrodes showed best suitability of PMC200* and PMN79 for Pd(II) determination. Recommendation of PMC200* electrode is in good agreement with our previously published results for simultaneous determination of Cd (II), Pb (II), Cu (II), and Hg (II) (Pikna, Heželová, and Kováčová 2015). In this case, there has been also confirmed applicability of voltammetry for the future environmental purposes.

Acknowledgement

This work was supported by the Ministry of Education, Science, Research and Sport of SR on behalf of the Agency of the Ministry of Education, Science, Research and Sport for EU structural funds, the project "Hydrogenation in liquid phase", ITMS project code 26220220144, Activity 2.1: Preparation and characterization of the support catalysts suitable for the hydrogenation in liquid phase, under the operational program Research and Development.

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