

# The effect of thermal treatment on the atomic structure of PtCu core-shell nanoparticles in PtCu/C electrocatalysts

**D B Shemet, V V Pryadchenko, V V Srabionyan, S B Belenov, A S Mikheykin, L A Avakyan, V E Guterman, L A Bugaev**  
Southern Federal University, Rostov-on-Don, Russia

E-mail: vvpriyadchenko@sfedu.ru

**Abstract.** Nanocatalysts PtCu/C with core-shell structure of PtCu nanoparticles were synthesized by the method of sequential chemical reduction of  $\text{Cu}^{2+}$  and Pt(IV) in carbon suspension, prepared on the basis of ethylene glycol–water solvent. The characterization of atomic structure of “as prepared” PtCu nanoparticles and obtained after thermal treatment at 350 °C was performed by Pt  $L_3$ - and Cu  $K$ -edge extended X-ray absorption fine structure (EXAFS), complemented with TEM and XRD studies. The processing of EXAFS was performed by the technique that enables to reduce the effect of correlations among fitting parameters on the determined values of local structure parameters of the absorbing atoms, which have the nearest surrounding consisting both Pt and Cu atoms.

## 1. Introduction

Among various important applications, the platinum nanoparticles (NPs) on carbon supports are a basic component of catalytic layers in low-temperature fuel cells. The main disadvantages of using these materials are i) insufficient corrosive and morphological stability of NPs, as well as of the metal-carbon composite itself during the operation and ii) relatively high cost. One of the key factors affecting the proton exchange membrane fuel cells (PEMFC) performance is the slow kinetics of the oxygen reduction reaction (ORR) under PEMFC operating conditions. An efficient way to overcome these problems and to obtain promising electrocatalysts for ORR is the synthesis of catalytic layer containing bimetallic NPs of composition PtM (where M – transition metal, such as Cu, Co, Ni, Ag etc.) with a core-shell structure (where shell is formed by Pt atoms and core - by M atoms) deposited onto highly developed surface of carbon supports [1,2].

In this work the structural study of PtCu/C electrocatalysts containing bimetallic PtCu NPs synthesized by sequential chemical reduction of components before and after thermal treatment was performed. The post-treatment is a quite simple method that enables to estimate the morphological stability of prepared materials. Moreover, in some cases the thermal treatment can improve the electrocatalytic activity of such materials [3]. In order to study the stability of the core-shell structure of PtCu NPs during the thermal treatment, the analysis of Pt  $L_3$ - and Cu  $K$ -edge XAS for “as prepared” and heated at 350 °C PtCu/C electrocatalysts was performed, complemented with TEM and XRD studies. The information on atomic structure of bimetallic PtCu NPs was derived from XAS spectra using the suggested fitting technique [4,2], which enables to reduce the effect of correlations between fitting parameters on the obtained values of structural parameters. Another fitting technique [5], which does not use Fourier transformation, was used to confirm the obtained values of structural parameters.

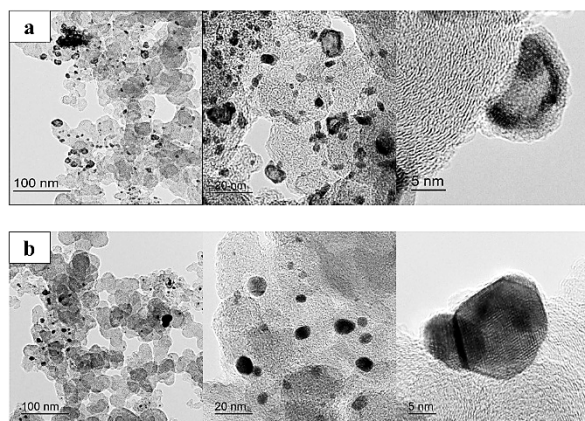


## 2. Experimental results.

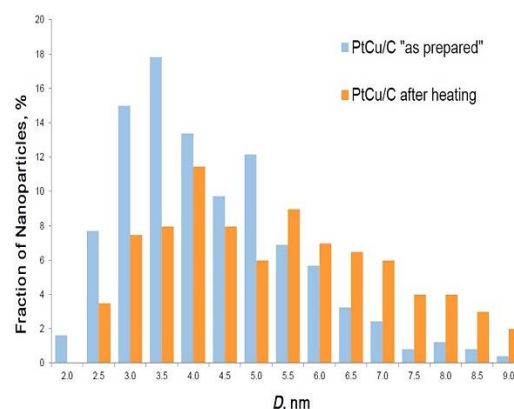
Carbon supported PtCu NPs were synthesized by the chemical reduction of Pt (IV) ( $\text{H}_2\text{PtCl}_6$ ) and  $\text{Cu}^{2+}$  ( $\text{CuSO}_4$ ) in a suspension of carbon powder (Vulcan XC72, Cabot), prepared on the basis of water-ethylene glycol solvent at  $\text{pH} = 10$  (an excess of  $\text{NH}_3$ ). The volume ratio of (water):(ethylene glycol) in the mixed solvent was 1:1. A 0.5 M solution of  $\text{NaBH}_4$  was used as a reducing agent. In order to synthesize core-shell PtCu NPs with the internal core of Cu atoms and the outer shell of Pt atoms, a method of sequential chemical reduction was used. First, nanostructured material Cu/C was obtained by the reduction of copper from the carbon slurry, prepared on the basis of  $\text{CuSO}_4$  solution. After that, the resulting Cu/C material was removed from the solution, washed and dried. Then, the obtained Cu/C composite was added to the aqueous solution of  $\text{H}_2\text{PtCl}_6$  containing an excess of  $\text{NH}_3$  ( $\text{pH} = 10$ ). After stirring, an excess of  $\text{NaBH}_4$  was added as a 0.5 M solution. The final material PtCu/C was separated by filtration, washed and dried for several hours in an oven at  $100^\circ\text{C}$ . A part of the resulting catalyst was heated at  $350^\circ\text{C}$  for 1 hour in an atmosphere of Ar.

The composition of the synthesized PtCu/C nanocatalysts corresponds to mass fraction of the metallic component of  $\sim 30\%$  by weight. The chemical composition was determined by x-ray fluorescence analysis using the x-ray spectrometer ARL OPTIM'X to be  $\text{Pt}_{0.8}\text{Cu}$  and remain quite stable during heating.

Microphotographs of the synthesized materials were obtained using a JEM-2100 (JEOL, Japan) microscope operated at an accelerating voltage of 200 kV and resolution of 0.2 nm. To conduct electron-microscopic studies a drop of specially prepared catalyst ink (about 0.5 mg of the catalyst was dispersed ultrasonically in 1 ml of isopropanol for 5 min) was applied on a copper grid covered with a thin layer of amorphous carbon film (to fix the microparticles on the surface) and dried for about 20 minutes in an air atmosphere at room temperature. TEM microphotographs and the histograms of particles' size distributions for "as prepared" catalysts and obtained after treatment are shown on Figures 1 and 2.



**Figure 1.** TEM microphotographs of PtCu/C electrocatalysts synthesized by sequential chemical reduction: "as prepared" (a) and after heating (b).



**Figure 2.** Histograms of NPs' size distributions in PtCu/C electrocatalysts.

Pt  $L_{3-}$  and Cu  $K$ -edge EXAFS spectra for the studied materials were measured at the  $\mu\text{Spot}$  beamline of the BESSY-II Synchrotron Radiation Facilities (Berlin, Germany). Mean electron current of a storage ring was maintained during experiment at 300 mA in Top-Up mode. The measurements were performed in the transmission mode utilizing a Si (111) channel-cut monochromator and two ionization chambers and diode for a reference channel. The photon energy scanning steps were adjusted to  $\delta E = 1.0$  eV and  $\delta k = 0.05$   $\text{\AA}^{-1}$  in the XANES and EXAFS regions respectively, where  $E$  is the energy of the incident radiation and  $k$  is the photoelectron wavenumber.

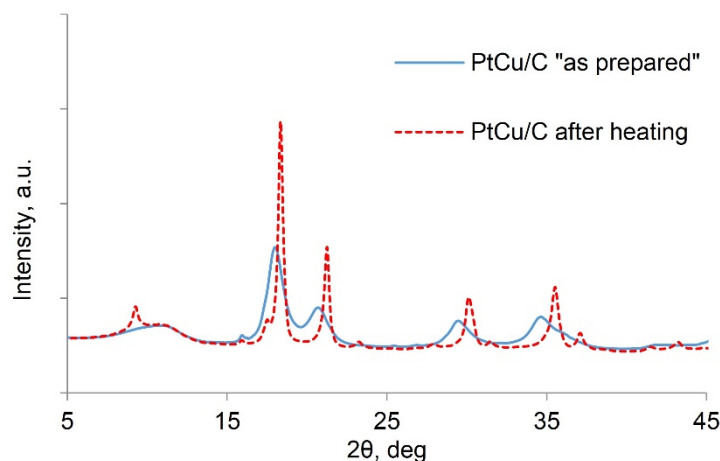
XRD Synchrotron X-ray powder diffraction patterns were collected at the BM01 beamline [6] of the Swiss-Norwegian Beamlines at European Synchrotron Radiation Facility (SNBL at ESRF, Grenoble, France). The monochromatic beam with a wavelength  $\lambda = 0.69489$   $\text{\AA}$  was used. The sample-to-detector

distance, the tilt angles of the detector and the wavelength were calibrated using LaB<sub>6</sub> NIST standard sample.

### 3. Discussion and conclusions

TEM microphotographs of “as prepared” electrocatalysts and obtained after thermal treatment are shown on Figure 1. As can be seen, there are NPs of different structures and sizes in “as prepared” materials. On the central image of Figure 1a (scale 20 nm) one can distinguish small homogeneous NPs (dark and light small spots), as well as a larger inhomogeneous NPs that could be attributed to the core-shell structures (light inner region with darker surface). One of such NPs is represented on right image of Figure 1a. After the thermal treatment, all NPs probably have similar structure, and besides, there are no evidences of the core-shell NPs on TEM images (homogeneous grey spots, Figure 1b). So the qualitative analysis of TEM images suggests that thermal treatment leads to the alloying of initially inhomogeneous NPs.

The histograms of particles’ size distributions derived from TEM micrographs are presented on Figure 2. To obtain good statistics, sizes of about ~1000 particles were measured for each sample. It can be seen, that the enlargement of NPs occurs as the result of thermal treatment at 350 °C. Observable bimodal character of size distributions can be explained by the presence of differently structured NPs in “as prepared” catalyst (see above), which are characterized by different size distributions.



**Figure 3.** XRD patterns of “as prepared” (blue solid line) and heated at 350 °C (red dashed line) PtCu/C electrocatalysts, synthesized by the method of sequential reduction of metals on a carbon support.

The increase in the average size of NPs as the result of heating is confirmed by the decrease of FWHM of XRD reflections, presented in Figure 3. Furthermore, Figure 3 shows that positions of the reflections are shifted toward higher values of  $2\theta$ , which indicates the decrease of the mean value of lattice parameter. Appearance of additional super-lattice reflections on XRD patterns at  $\sim 9^\circ$ ,  $17^\circ$ ,  $23^\circ$ ,  $28^\circ$  etc. indicates the presence of the long-range order in alloyed NPs [3,7].

In Figure 4 the magnitudes of the Fourier-transforms  $|F(R)|$  of experimental and theoretical Cu *K*- and Pt *L*<sub>3</sub>-edge EXAFS are compared. The fit of the Fourier-transforms  $F(R)$  of EXAFS spectra was performed using the following expression for oscillatory parts  $\chi(k)$ :

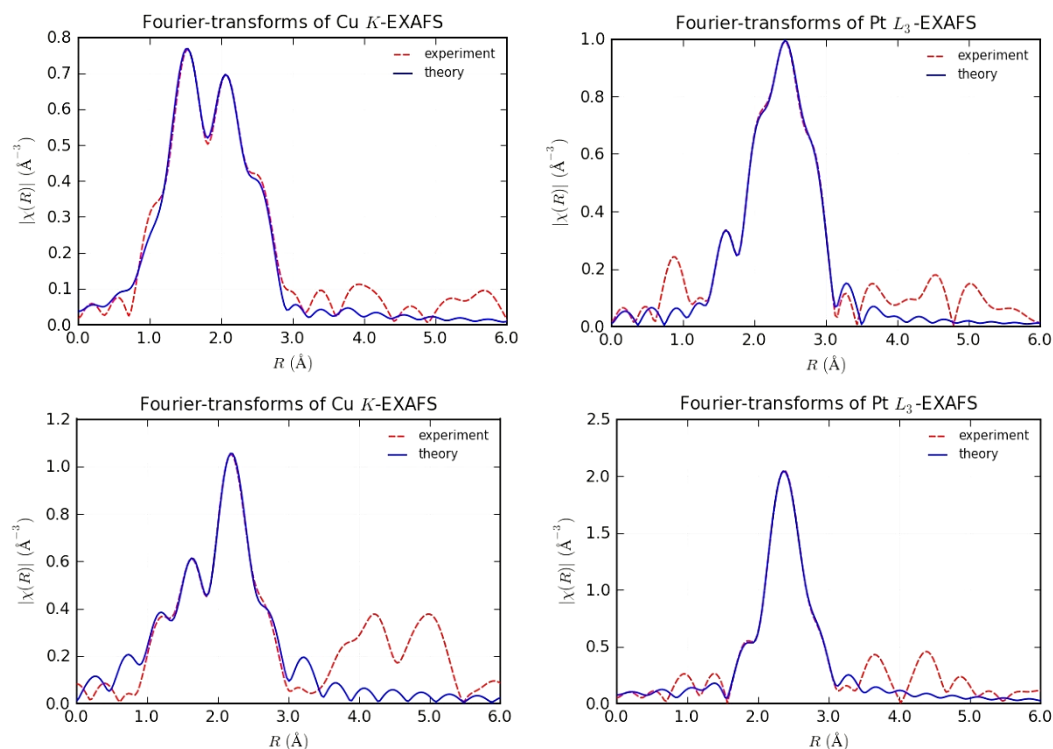
$$\chi_{\text{Pt}}(k) = S_0^2 (N_{\text{Pt-Pt}} \cdot \chi_{\text{Pt-Pt}} + N_{\text{Pt-Cu}} \cdot \chi_{\text{Pt-Cu}}) \quad (1)$$

$$\chi_{\text{Cu}}(k) = S_0^2 (N_{\text{Cu-Cu}} \cdot \chi_{\text{Cu-Cu}} + N_{\text{Cu-Pt}} \cdot \chi_{\text{Cu-Pt}}) \quad (2)$$

where  $\chi_{\text{Pt-Pt}}$ ,  $\chi_{\text{Pt-Cu}}$ ,  $\chi_{\text{Cu-Cu}}$ ,  $\chi_{\text{Cu-Pt}}$  – the contributions in  $\chi(k)$ , which correspond to photoelectron scattering processes on a one nearest atom of a specific type (the first label in subscript indicates the absorbing atom and the second label indicates the scattering one). Determination of structural parameters for the nearest neighbors of the absorbing atoms was performed by Fourier-transform analysis of EXAFS using the shortened *k*-range with  $k_{\text{min}} \sim 6 \text{ \AA}^{-1}$ , which is sufficient for the used number of number of fitting parameters [8] and enabled to neglect the contribution of photoelectron multiple

scattering processes and backscattering on the light atoms (carbon atoms of the support and oxygen atoms) [9,4].

The fit gave the average values of structural and non-structural parameters: partial coordination numbers  $N_{\text{Pt-Pt}}$ ,  $N_{\text{Pt-Cu}}$ ,  $N_{\text{Cu-Pt}}$ ,  $N_{\text{Cu-Cu}}$  and corresponding Debye-Waller parameters  $\sigma^2_{\text{Pt-Pt}}$ ,  $\sigma^2_{\text{Pt-Cu}}$ ,  $\sigma^2_{\text{Cu-Pt}}$ ,  $\sigma^2_{\text{Cu-Cu}}$ , interatomic distances  $R_{\text{Pt-Pt}}$ ,  $R_{\text{Pt-Cu}}$ ,  $R_{\text{Cu-Pt}}$ ,  $R_{\text{Cu-Cu}}$  and energy-shift parameters  $e_0(\text{Pt})$ ,  $e_0(\text{Cu})$  [10]. One of the criteria of correctness of the fit results was the coincidence of parameters  $\sigma^2_{\text{Pt-Cu}}$  with  $\sigma^2_{\text{Cu-Pt}}$  and  $R_{\text{Pt-Cu}}$  with  $R_{\text{Cu-Pt}}$ .



**Figure 4.** Experimental (red dashed lines) and theoretical (blue solid lines) magnitudes of the Fourier-transforms of Cu K- and Pt  $L_3$ -edge EXAFS for “as prepared” (top panel) and heated at 350 °C (bottom panel) PtCu/C electrocatalysts.

The obtained values of local structure parameters for Pt and Cu atoms in bimetallic PtCu NPs are shown in Table 1. Small values of partial coordination numbers of Cu indicate that a significant fraction of Cu atoms are presented in oxide form in PtCu/C, which is, however, amorphous at both temperatures and therefore cannot be seen in XRD. Increase of the total coordination number of Cu is probably due to the reduction of Cu ions during thermal treatment [11].

One more source of structural information are the interatomic distances  $R_{\text{Pt-Pt}}$ ,  $R_{\text{Pt-Cu}}$  и  $R_{\text{Cu-Cu}}$ . In “as prepared” NPs their values correspond to those obtained recently for the core-shell NPs [2], whereas after heating the values of interatomic distances become almost equal. The latter is not typical neither for NPs with homogeneous solid solution structure nor with core-shell structure, but is an evidence in favor of the above assumption on the presence of local order in NPs, which is typical for intermetallic compounds [7].

Table 1. Values of local structure parameters of Pt and Cu atoms in bimetallic PtCu nanoparticles

Sample	$R, \text{\AA} (\pm 0.01)$			$\sigma^2, \text{\AA}^2 (\pm 0.001)$			Partial coord. numbers			
	$R_{\text{Pt-Pt}}$	$R_{\text{Pt-Cu}}$	$R_{\text{Cu-Cu}}$	$\sigma^2_{\text{Pt-Pt}}$	$\sigma^2_{\text{Pt-Cu}}$	$\sigma^2_{\text{Cu-Cu}}$	$N_{\text{Pt-Pt}}$	$N_{\text{Pt-Cu}}$	$N_{\text{Cu-Pt}}$	$N_{\text{Cu-Cu}}$
“As prepared” PtCu/C	2.74	2.64	2.54	0.007	0.009	0.007	8.4	2.2	1.9	1.9
Heated at 350 °C	2.66	2.64	2.64	0.005	0.005	0.009	8.3	3.4	3.0	3.6

For detailed understanding of significant structural changes in PtCu NPs between room temperature and 350 °C, further structural investigations of PtCu/C electrocatalysts at different temperatures from these interval required.

#### 4. Acknowledgements

The work was supported by Grant of Southern Federal University (№ 213.01-07.2014/10ПЧБГ). We thank SNBL at ESRF for providing beamtime for XRD measurements and my-Spot beamline at BESSY II for providing beamtime for EXAFS measurements.

#### 5. References

- [1] Salgado J R C, Antolini E and Gonzalez E R 2005 Carbon supported Pt<sub>70</sub>Co<sub>30</sub> electrocatalyst prepared by the formic acid method for the oxygen reduction reaction in polymer electrolyte fuel cells *J. Power Sources* **141** 13–8
- [2] Pryadchenko V V, Srabionyan V V, Mikheykina E B, Avakyan L A, Murzin V Y, Zubavichus Y V., Zizak I, Guterman V E and Bugaev L A 2015 Atomic Structure of Bimetallic Nanoparticles in PtAg/C Catalysts: Determination of Components Distribution in the Range from Disordered Alloys to “Core–Shell” Structures *J. Phys. Chem. C* **119** 3217–27
- [3] Xiong L and Manthiram A 2005 Effect of atomic ordering on the catalytic activity of carbon supported PtM (M = Fe, Co, Ni, and Cu) alloys for oxygen reduction in PEMFCs *J. Electrochem. Soc.* **152** A697–703
- [4] Srabionyan V V., Bugaev A L, Pryadchenko V V., Avakyan L A, van Bokhoven J A and Bugaev L A 2014 EXAFS study of size dependence of atomic structure in palladium nanoparticles *J. Phys. Chem. Solids* **75** 470–6
- [5] Pryadchenko V V., Galustov A D, Srabionyan V V. and Bugaev L A 2014 Determination of the local atomic structure of material from X-ray absorption spectroscopy data without fourier analysis of experimental spectra *Opt. Spectrosc.* **117** 187–93
- [6] Dyadkin V, Pattison P, Dmitriev V and Chernyshov D 2016 A new multipurpose diffractometer PILATUS@SNBL *J. Synchrotron Radiat.* **23** 825–9
- [7] Oezaslan M, Hasché F and Strasser P 2012 PtCu<sub>3</sub>, PtCu and Pt<sub>3</sub>Cu Alloy Nanoparticle Electrocatalysts for Oxygen Reduction Reaction in Alkaline and Acidic Media *J. Electrochem. Soc.* **159** B444–54
- [8] Bugaev L a., Avakyan L a., Srabionyan V V. and Bugaev a. L 2010 Resolution of interatomic distances in the study of local atomic structure distortions by energy-restricted x-ray absorption spectra *Phys. Rev. B - Condens. Matter Mater. Phys.* **82** 1–9
- [9] Srabionyan V V., Bugaev A L, Pryadchenko V V., Makhboroda A V., Rusakova E B, Avakyan L A, Schneider R, Dubiel M and Bugaev L A 2013 EXAFS study of changes in atomic structure of silver nanoparticles in soda-lime glass caused by annealing *J. Non. Cryst. Solids* **382** 24–31
- [10] Koningsberger D C, Mojet B L, van Dorssen G E and Ramaker D E 2000 XAFS spectroscopy; fundamental principles and data analysis *Top. Catal.* **10** 143–55
- [11] Lee S Y, Mettlach N, Nguyen N, Sun Y M and White J M 2003 Copper oxide reduction through vacuum annealing *Appl. Surf. Sci.* **206** 102–9