A NEW ROUTE FOR SYNTHESIS AND CHARACTERIZATION OF MACROPOROUS GRANULAR SILVER

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S-a eleborat un procedeu eficient şi nepoluant de sinteză a argintului macroporos granular prin reducerea Ag_2SO_4 cu acid ascorbic, în fază heterogenă în mediu apos. Procedeul elaborat este cumparat cu procedee similare realizate prin reducerea cu acid ascorbic a $AgNO_3$, şi respectiv a AgNO. Probele au fost examinate la microscopul optic şi caracterizate prin analiză XRD. Au fost estimate porozitatea şi proprietăţile lor electroconductive. Argintul granular microporos obtinut a fost caracterizat prin analiză FTIR, TG-DSC, TEM şi testat drept catod într-o celulă de electroliză în soluţie de KOH comparativ cu un catod din argint masiv. Conductivitatea electrică bună şi suprafaţa specifică mare a produsului ar putea permite utilizarea acestuia în electrochimie.

An effective and green route was elaborated for synthesis of macroporous granular silver by reduction of Ag_2SO_4 with ascorbic acid in heterogeneous phase in aqueous medium. The synthesis method was compared with similar procedures using the reduction of $AgNO_3$ or $AgNO_2$ with ascorbic acid. The samples were examined by optical microscopy, XRD patterns as well as porosity and electroconductive properties.The product was characterized by FTIR, TG-DSC, TEM and tested as cathode in an electrolysis cell in KOH solution comparative to a bulk silver cathode. The good electric conductivity and high specific aria of the product may sustain its electrochemical use.

Keywords: macroporous, heterogeneous, silver salts

1. Introduction

Silver has specific uses based on some distinguished properties like these: is the metal with the best electrical and thermal conductivity, even though it is not bulk [1], has very strong antibacterial [2], antiviral [3] and antifungal [4] effects, is a

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catalyst in the direct epoxidation of olefins with molecular oxygen. There are many methods of silver compounds reduction to obtain metallic powders, porous materials or nanoparticles. Silver nanoparticles for antimicrobial purposes are usually prepared by reduction of silver nitrate diluted solutions with different reducing agents in the presence of organic compounds with protection function [5]. By varying the temperature, reactants concentration, composition and concentration of protective substances, it can adjust size and shape of nanoparticles [6], [7]. By controllable growth of silver nanoparticles, it can obtain nanowires [8].

Silver powders for electroconductive coatings are obtained suchlike nanoparticles, but working with greater concentrations of silver nitrate, with or without protective compounds or by hydrogen reduction of silver oxide [9].

Macroporous silver was prepared by metallurgical or chemical methods. Metallurgical methods - to obtain pellets with 54-56 % relative densities- imply sinterization of submicron silver powders in the presence of a binding agent[10] or, - in need of greater porosities - using a supplementary pulverulent material which is subsequently discard by heating [11]. Chemical methods imply the use of a sacrificial solid template [12] prepared by adsorption of silver nitrate on activated charcoal, followed by sodium borohydride reduction and burning of the carbon template in air. Other methods use an excess of a soft template with reducing power (Triton X-114 surfactant [13]), imply the thermal decomposition of a dextran gel in which is incorporated silver nitrate [14] or prolonged heating of a silver nitrate solution in ethylene glycol [15, 16]. Macroporous silver is used for electrodes in some electrochemical cells, after anodic oxidation to silver oxide [17]. Silver nitrate is frequently used as silver precursor in chemical methods, being preferred to other compounds due to the high solubility in water and organic polar solvents. Agents like sodium borohydride, hydrazine or ethylene glicol are frequently used for silver nitrate reducing.

Ascorbic acid (**AA**) reacts with $AgNO_3$ in diluted solutions, method being used to assay **AA** in animal tissues [18]. Silver nanoparticles (27 nm) were prepared by reaction of 0,2 M silver nitrate solution with 4 M ascorbic acid solution at 40^oC without the assistance of any surfactant [19]. Silver nanorods and nanowires have been synthesized by using a 4 mM silver nitrate solution with SDBS (2 mM) and a 10 mM ascorbic acid solution [20] . Stable dispersions of silver nanoparticles were prepared using medium concentrate reagents $AgNO_3$ (0,3 M), **AA** (0,25 M) in aqueous solutions and Daxad 19 as stabilizating agent [21]. Different morfologies of silver particles, both isometric and anisotropic have been prepared with the same reagents, but varying the conditions [22]. Silver particles (223-1149 nm) were prepared in the reaction of $AgNO_3$ (0,183-0,167 M) with **AA** (0,167-0,666 M) in the presence of arabic gum as stabilizating agent [23]. Flower-like silver nanoplate micro-assemblies were synthesized by reaction of $AgNO_3$ (10 mM) with **AA** (10 mM) in the presence of PVP (0,171 mM) at 150^oC [24]. Nanostructures assemblies

were synthesized in solution by the reaction of $AgNO_3$ (0,1 M) with **AA** (0,1 M) with or without addition of some organic acids [25][26][27]. Silver depositions with (0,46-4,43) x 10^{-5} Ωm resistivity were obtained by ink-jet method using 67% silver nitrate solutions (pH 7-7,2) and 40% ascorbic acid solution (pH 6,5) [28].
This paper proposes a new route for synthesis of macroporous granular silver by reduction of silver sulphate with ascorbic acid in heterogeneous phase.The synthesis method was elaborated after the preliminary investigation of the silver salts ($AgNO_3$, $AgNO_2$ or Ag_2SO_4) behavior in reduction reaction with ascorbic acid (**AA)** in aqueous medium. High concentrations of reagents (300g/l solution in the case of $AgNO_3$) or the heterogenous medium with a small amount of water in the case of relatively difficult soluble silver salts, like $AgNO_2$ or Ag_2SO_4 have been used in reactions. Solid **AA** was progressively added in the conditioned silver salts to obtain an elevated concentration of reducing agent.
The macroporous silver powder obtained has been characterized by optical microscopy, XRD, FTIR, TG-DSC, TEM , as well as by electrochemical properties.

2. Experimental

a. ***Preliminary experiments***

Reaction of $AgNO_3$ with AA
Macroporous silver was obtained in the reaction of $AgNO_3$ concentrated solution with **AA**. Exothermic reaction starts at room temperature after progressively adding of ascorbic acid. A high concentration of nitrogen oxides and nitric acid determined the interruption of the reaction and the decrease of the efficiency (at about 29%).The adding of a great excess of AA does not increase the reaction efficiency.
Ionic silver that has remained in the solution after filtration of primary silver was recovered by precipitation with an excess of KOH solution and filtration.

Reaction of Ag_2SO_4 with AA
An excess of ascorbic acid was progressively added to a paste of silver sulphate (min. 99.8% P.O.Ch.-Gliwice) in water (2 mol Ag_2SO_4 for 1 l water).The reaction was exothermic. After the closing of the exothermic reaction, the macroporous silver obtained was separated by filtration, washed two times with water, picked up in boiling water and filtrated.
Ionic silver that has remained in the acidic solution was recovered by precipitation and filtration after the alkalinization with KOH solution.
Efficiency in macroporous silver (gravimetric calculated after drying of product) was about 94%. Comparatively with reaction realized with $AgNO_3$ no direct oxidant effect of H_2SO_4 concentration increase was observed, but the increase in concentration of H_2SO_4 limited the reaction efficiency.

Reaction of $AgNO_2$ with AA

$AgNO_2$ crystalline commercially salt (min. 99%, *Merck*) in water (4 mol for 1 l water) or a mixture of saturated solution in equilibrium with acicular crystals formed by crystallization at room temperature of a supersaturated solution of salt in water have been used in the reduction reaction with **AA**. In both cases, reaction was exothermic. HNO_2 formed was quickly decomposed in nitrogen oxides. Comparatively with both foregoing reactions, this reaction is complete (efficiency ~ 100%), due to the quick decomposition of HNO_2.

Synthesis of macroporous granular silver by the reduction of Ag_2SO_4 with AA

Reactive: - microcrystalline Ag_2SO_4 (min. 99, 5%, *Riedel de Haen*) and ascorbic acid (min. 99.7%, Merck).
A heterogeneous mixture of 6,236 g Ag_2SO_4 (0.02 mol) in 10 mL water reacts with 3.646 g ascorbic acid (0.0207 mol).
At the end of exothermic reaction, the mixture obtained was heated to boiling. The crude macroporous silver obtained was treated again, two times, with an excess of a mixture (0.352 g ascorbic acid in 10 ml water), heated to boil with 25 mL water and filtered. The final solid product obtained was dried 30 min in an oven at 120 ^oC (yield 96.2%). A 98.5% yield was obtained with greater amount of reagents.
The final powder (macroporous granular silver) was examined on a *MC5A microscope* and *electroconductive properties* were estimated with a *Fluke 289* multimeter by resistance measuring of a slowly pressed material column in a tube glass (23 cm length and 8.1 mm internal diameter) connected with multimeter by silver discs; apparent density was calculated after weighing the tube with material. Grinded samples were analyzed by *X-ray diffraction* in a *Rigaku Miniflex 2* diffractometer (2θ = 0-70^o) and data processing with *Match - Crystal Impact* software. *TEM images* were obtained using a *Philips CM 20* model.
FTIR spectra were registered on *Tensor 27 – Bruke apparatus* using KBr pellets, in 400-4000 cm^{-1} domain. *TG-DSC* analysis was determined on *STA 449C – Netzsch* apparatus in 30-900^{o}C range, in argon.
The product, in a 35% potassium hydroxide solution, was assayed as cathode in an electrolysis cell comparative to a bulk silver cathode with similar size (8.5cm height, 8.2 mm diameter); the cathode space was delimitated by the anodic compartment by 56 cm^2 Nafion® NR212 membrane; as anode, a 34 mm diameter coaxial mesh (W1.4306- 0.2 mm, field dimensions 30x30 μm) was disposed near the membrane.

3. Results and discussions

Optical microscopy

The microscopy imagine of silver product obtained using Ag_2SO_4 (paste in water) is presented in Fig.1 and is similar with that obtained using $AgNO_2$ crystalline salt.(Fig.1).

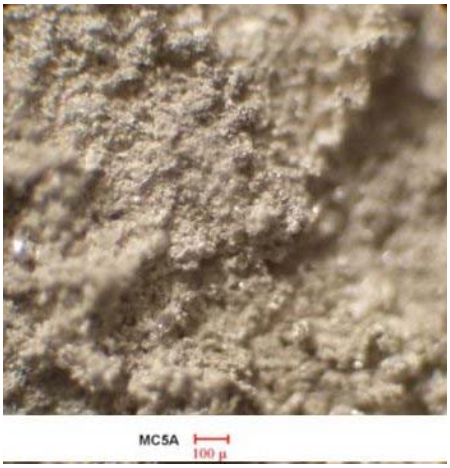

Fig. 1. Microscopy imagine of silver product obtained in reaction of Ag_2SO_4 (paste in water) with AA

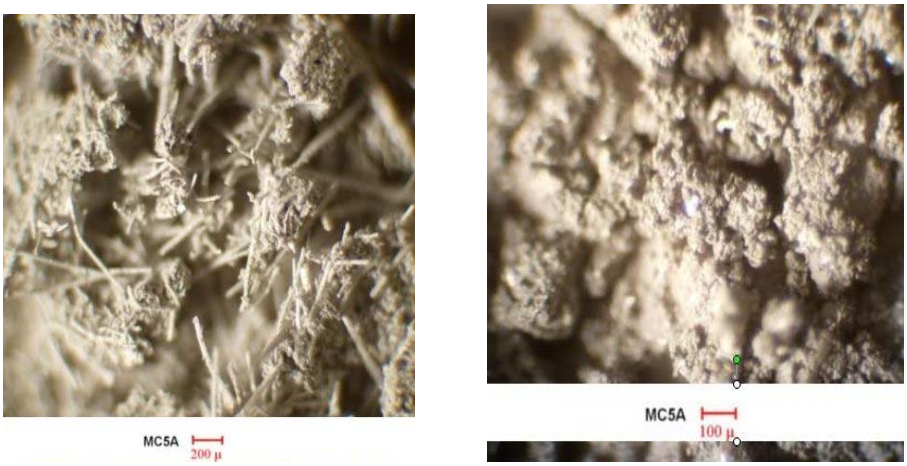

Fig.2. Microscopy imagine of the silver product obtained using a mixture of $AgNO_2$ saturated solution in equilibrium with acicular crystals (left) and of the grey powders precipitated from the residual solutions (right).

The microscopy imagine of the silver product obtained using a mixture of $AgNO_2$ saturated solution in equilibrium with acicular crystals shows macroporous silver and silver filamentous microwires, suggesting that the reaction takes place mostly at the interface of the solution with the salt crystals.

The silver powders obtained from the acid residual solutions (by $AgNO_3$ or Ag_2SO_4 reduction with AA) have been washed with boiling water and dried at room temperature. The aspect (Fig.3) of these powders (observed at the optical microscope) is more fine, with an apparent density of 1,646 g/cm^3 (15,7% of *bulk*) and higher electrical resistivity (3, 16 ^{x} 10^{-2} Ωm in comparation with 1,991 ^{x} 10^{6} Ωm of *bulk* and 1564 Ωm of the primary product.). The microscopic aspect and their poor conductivities suggest the presence of silver oxides in mixture with the fine silver powders. By subsequent reduction with solutions of **AA**, washing and drying, they give products with a silvery aspect and good electric conductivity.

The effect of a weak organic agent protector like polypropylene glycol (**PPG**-liquid oligomers mixture) in the reaction of crystalline Ag_2SO_4 with **AA** has been also tested. The addition of 15% **PPG** in water give a mixture of macroporous granular silver and fine silver powders. In the absence of **PPG**, beside macroporous silver, little extent of crystalline silver powder with a great particulate dimension result. Working with a mixture of **PPG** and reagents in the absence of water, reaction take place only at the surface of Ag_2SO_4 crystals where silver was deposited and do not progress in the mass of crystals neither of solvent boiling.

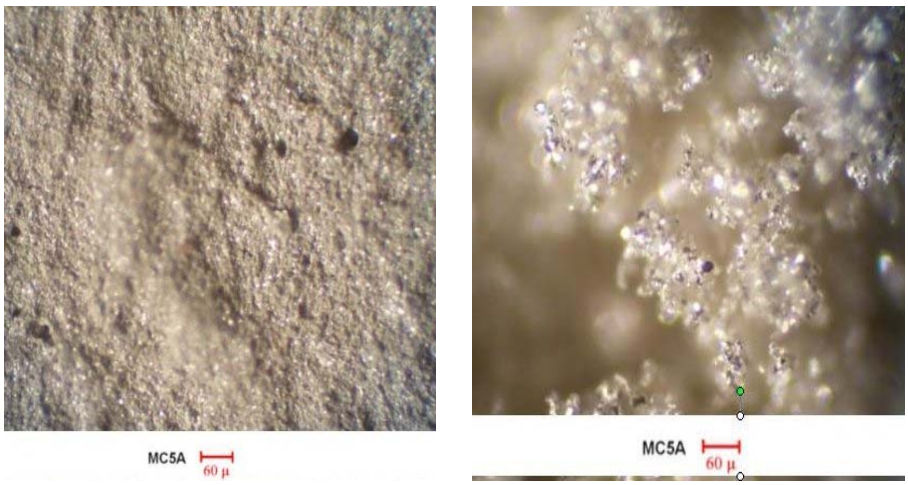

Fig.3. Fine silver powder obtained with 15% PPG (left); crystalline silver powder obtained without PPG (right)

XRD analysis

XRD diagrams of macroporous silver obtained by $AgNO_3$ and Ag_2SO_4 reduction, of powders obtained from the acid residual solutions and of the product of subsequent reduction of these powders with **AA** show the following:

- macroporous silver obtained after a single treatment with **AA** is unpurified with traces of silver oxides containing also Ag_2SO_4 when this was used as precursor.
- Silver obtained by $AgNO_2$ reduction does not contain impurities.
- The powders obtained after KOH alkalinization was contaminated with a great content of oxides and silver salts.
- Subsequent treatment with **AA** of the macroporous crude silver obtained from $AgNO_3$ or Ag_2SO_4 or of the powders obtained after KOH alkalinization of the acid residual solutions gives pure silver products.
- Both the macroporous primary products and subsequent reduced recovery silver powders have silvery aspect with metallic reflexions, good electrical conductivities and adsorbent properties.

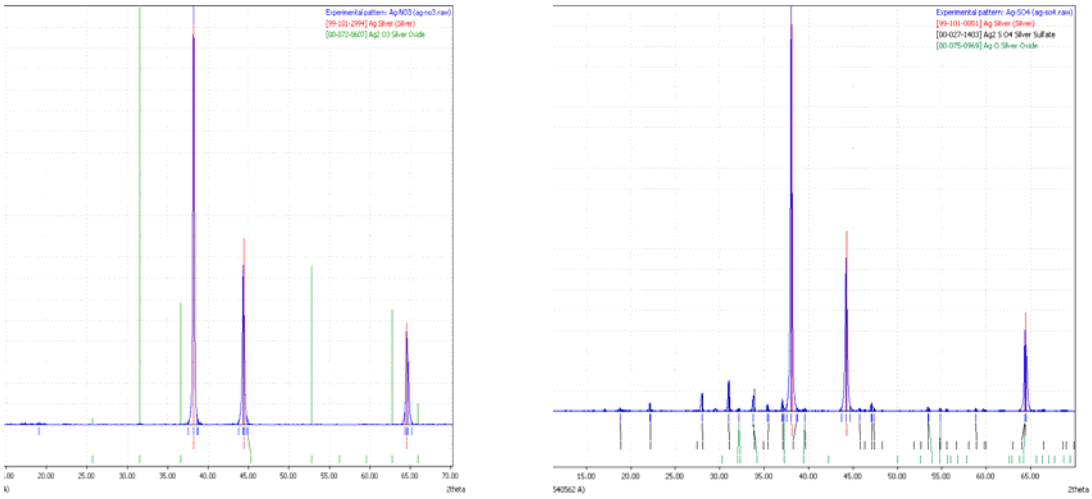

Fig.4. XRD for primary products obtained by reduction of $AgNO_3$ (left) and Ag_2SO_4 (right) with AA

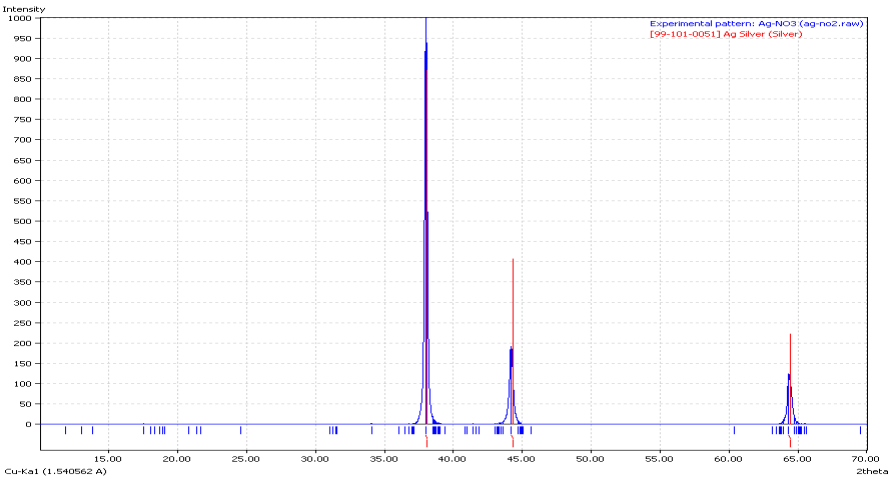

Fig. 5. XRD for the product obtained by reduction of $AgNO_2$ with AA

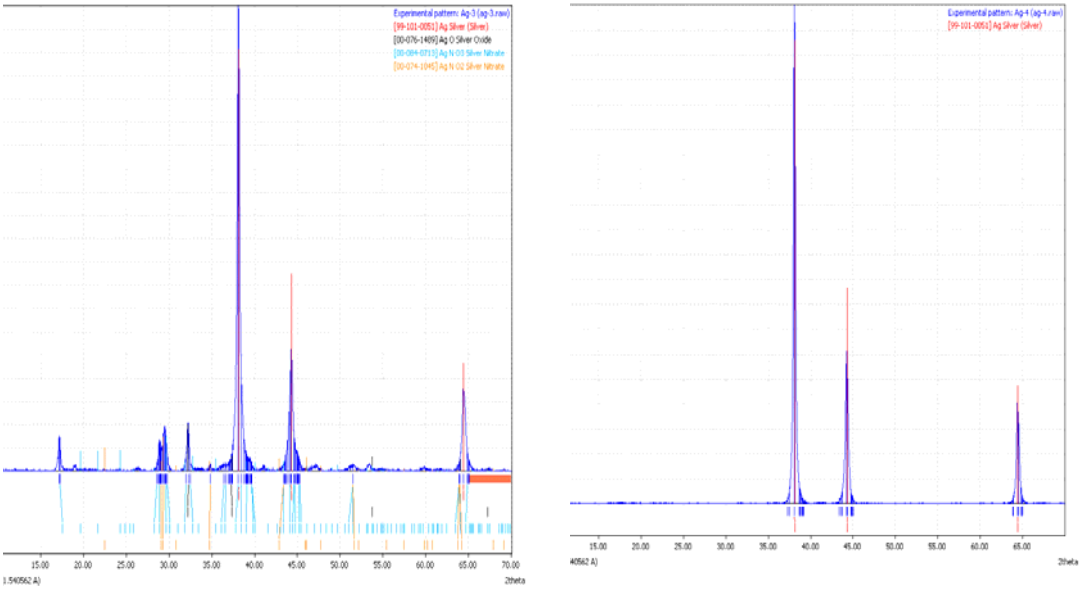

Fig.6. XRD for powders obtained after alkalinization (left); powders treated with AA (right)

The macroporous granular silver synthesized by the reduction of Ag_2SO_4 with AA is granular, being easy to crash in small fragments. The granules are composed of micron subunities with pores of similar size. Apparent density of product is 1.397 g/cm^3, (13.3% of *bulk*), resulting an estimated porosity of 86.7%. Estimated resistivity of product is 2.02×10^{-5} (1270 Ωm of *bulk*).

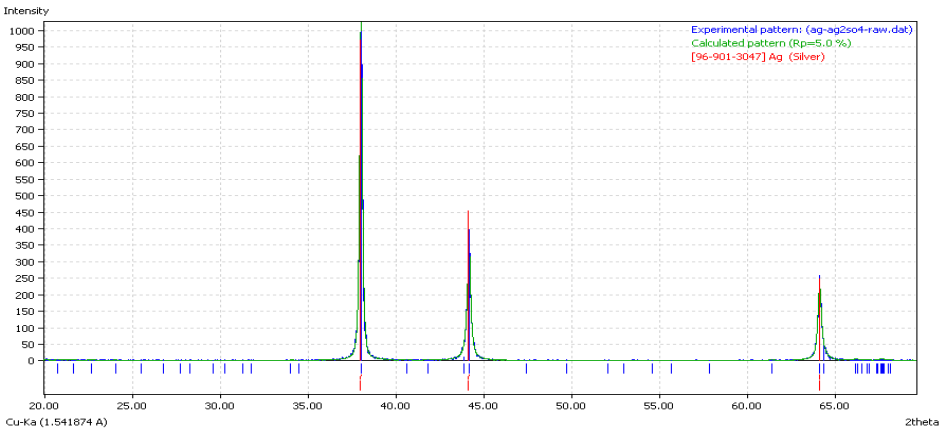

Fig.7. XRD of macroporous silver obtained by reduction of Ag_2SO_4 with AA

XRD diagram shows peaks with 2θ values of 38°, 44°, 64° corresponding to crystal planes (111), (200) and (220) of fcc silver, by diffraction data resulting a medium crystallite size of 39.29 nm.

TG-DSC analysis

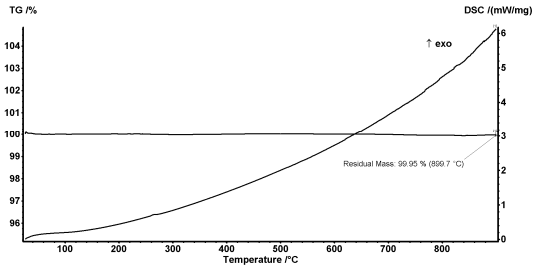

Fig.8. TG-DSC curves for the microporous silver obtained by reduction of Ag_2SO_4 with AA

The thermal analysis confirmes the purity of the product – after heating at 900^{0}C it remains practically unchanged (final mass = 99.95%).

TEM analysis

Silver granules are composed by aggregated of primary polydisperse nanoparticles with prevalent spherical or oval shapes. Nanowires are also present in aggregates, facilitating the connections. HRTEM images reveal some spherical MTP (multiply twinned particles).

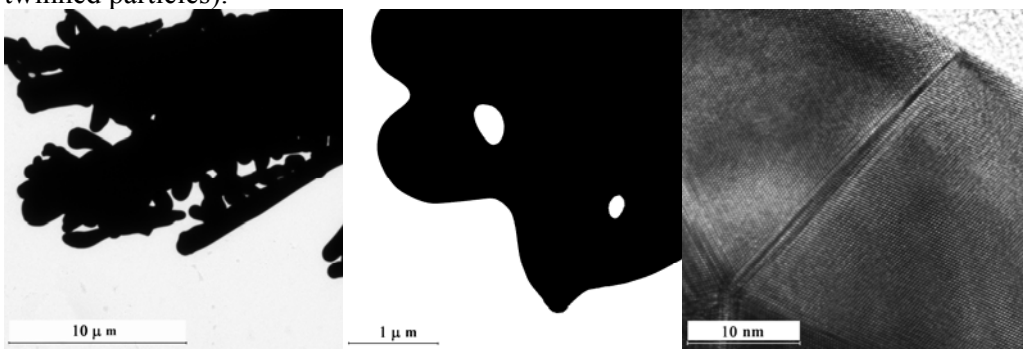

Fig.9.TEM images of granular silver. Left- aggregated nanoparticles with nanowires; center- image detail; right- HRTEM image of a MTP.

FTIR spectrum shows only traces of ascorbic acid in the product.

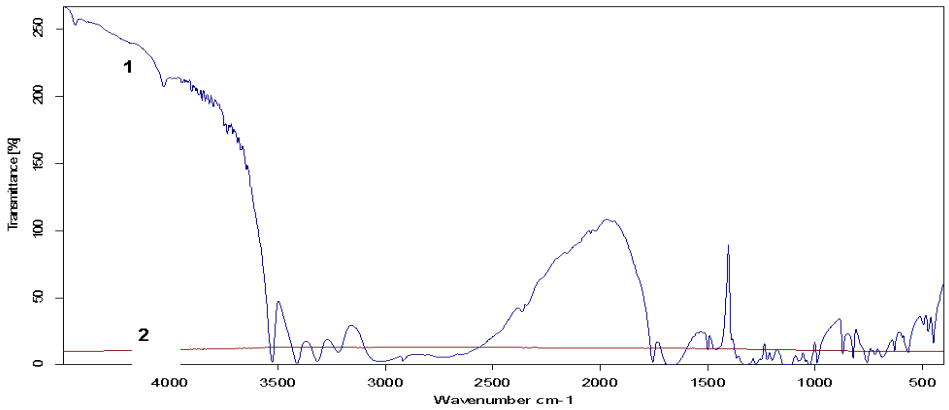

Fig.10. FTIR spectra of AA (2) and of the silver product (2)

Assay of the product in the electrolysis cell

A better efficiency was done working with the macroporous silver cathode comparative to the bulk silver cathode for I > 1.5A (6,85 A/dm^2).

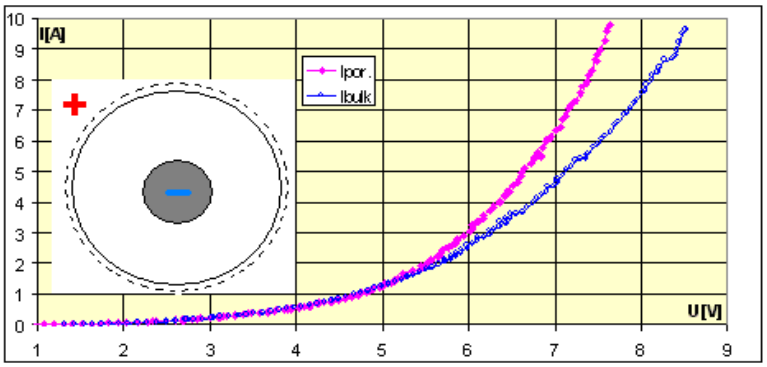

Fig.11.(U) diagrams in an electrolysis cell with a cathode as porous silver (8.5cm height, 8.2 mm diameter) and bulk silver cathode and coaxial membrane and anode

4. Conclusions

The new synthesis procedure of macroporous silver, described in this paper, uses the reduction reaction of Ag_2SO_4 with an excess of ascorbic acid, forming a pure product, with high yield, without the generation of noxious gases. The ionic silver impurities of the crude product are quickly reduced by a successive treeatment with ascorbic acid. The fine silver powder may be recovered by KOH alkalinization of the residual solution. The better efficiency of the product (compared to bulk silver) as cathode in water electrolysis suggests its potential electrochemical use.

REFERENCES

1. *R.F. Berg, G.G. Ihas*, Rev. Sci. Instrum., **1984**, 55, 1174.
2. *J.R. Morones*, et al, Nanotechnology, **2005**, 16, 2346-2353.
3. *J.L. Elechiguerra, et al*, J. Nanobiotech., **2005**, 3, doi: 10.1186/1477-3155-3-6
4. *K.J.Kim, et al*, J. Microbiol. Biotechnol., **2008**, 18, 1482-1484.
5. *I. Sandu, et al*, Romanian Patent 105551 B1, **1992**.
6. *Y. Sun , Y. Xia*, Science**, 2002**, 298, 2176-2179.
7. *L. Zhongchun*, et al, Cryst. Res. Technol., **2009**, 44, 841-844.
8. *J. Zhou, et al*, Mater. Sci.-Poland, **2009**, 27, 73-78.
9. *F. Montino, L. Colombo*, U. S. Patent 4039317, **1977**.
10. *E.A. Oliber, et al*, Matéria, **2003**, 8, 350-357.
11. *C.C. Balke, D. Hill*, U. S. Patent 2672415, **1954**.
12. *J. Yan , et al*, Mater. Sci. Forum, **2006**, 510, 770-773.
13. *F. Khan, M. Eswaramoorthy*, C.N.R. Rao, Solid State Sci**., 2007**, 9, 27-31.
14. *D. Walsh, et al*, W.O.Patent 054710, **2004**.
15. *J. Du, D.J. Kang*, Mat. Lett., **2008**, 62, 3185–3188.
16. *M.A. Barteau*, Surface Sci., doi:10.1016/j.susc.2006.09.024.
17. *L.J. Gaudino*, U. S. Patent 4930211, **1990**.
18. *J. Gough*, Biochem. J., **1933**, 27, 1279-1286.
19. *M.K. Motlagh, et al*, J. Iran. Chem. Soc., **2010**, 7, S113-S122.

20. *J. Zhou, et al*, Mater. Sci.-Poland, **2009**, 27, 73-78.
21. *I. Sondi, et al*, J. of Colloid and Interf. Sci., **2003**, 260, 75–81.
22. *L. Suber, et al*, J. of Colloid and Interf. Sci., **2005**, 288, 489–495.
23. *K.P. Velikov, et al*, Langmuir, **2003**, 19, 1384-1389.
24. *X. He, et al*, Mater. Sci. Forum, **2011**, 675-677, 299-302.
25. *B. Zhang, et al*, J. of Mater. Chem., **2011**, 21**,** 2495-2501.
26. *F. Tomoyuki, I. Hiroaki,* J. Cryst. Growth, **2002**, 241, 193-199.
27. *W. Songping, M. Shuyuan*, Mater. Chem. & Phys., **2005**, 89, 423-427.
28. *S.M. Bidoki, et al*, J. Micromech. Microeng., **2007**, 17, 967–97.