Bulgarian Chemical Communications, Volume 50, Special Issue A (pp. 114- 118) 2018

Nanosized Ag particles as catalyst in gas-diffusion electrodes for ORR

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Received September 11, 2017; Accepted November 29, 2017.

Silver nanosized particles were prepared via original process. The obtained silver particles size varied between 10 to 50 nm with a shape that was mainly spherical. The UV-visible spectroscopy investigation showed Plasmon resonance peak at between 440 and 470 nm for silver nanoparticles. Transmission electron microscopy study showed hexagonal and cubic crystal structures of silver particles.In order to verify the catalytic activity of the obtained silver nanoparticles they were incorporated in the active layer of the air gas-diffusion electrodes. The active layer of the gas diffusion electrode was prepared via four methods. The catalyst activity of these electrodes was studied in three-electrode half-cell with Ag/AgCl reference electrode using 4M NaCl solution as electrolyte. The results obtained showed stable operation of all electrodes up to 50 mA/cm^2, and for some – even up to 100 mA/cm^2.

Key words: Ag nanosized particles, Ag catalyst, air gas-diffusion electrodes

INTRODUCTION

During the recent years there is increased scientific interest toward the synthesis of nano materials and their applications. In the scientific literature there are many different applications of metal nanoparticles in areas such as electronics, optics and medicine. Recently, they are also used as catalysts [1], electrode materials for lithium ion batteries [2] as well as in the development of solar cells [3]. There are different methods for the production of silver nanoparticles [4], among them electrochemical methods [5], photocatalytic techniques [6] and chemical methods, particularly those using external energy fields, the most common being ultrasound [7] or microwaves [8].

Depending on the synthesis method and the working conditions, the resulting silver nanoparticles may have different sizes and shapes (spheres, cubes, tetrahedra, fibers, etc.).

Silver is known as one of the best catalysts for the electrochemical reduction of oxygen in an alkaline electrolyte [9-11]. Furthermore, silver appears to present a great catalytic activity for the heterogeneous decomposition of H_2O_2. H_2O_2 is generated during the operation of air electrode. Part of it decomposes to H_2O and ½ O_2 in the pore volume of the electrode. This oxygen oxidizes chemically the carbon surface and it is the main reason for disruption of hydrophobic properties of carbon catalysts. This phenomenon leads to increased difficulties of the oxygen's transportation toward the electrochemically active centers of the catalyst and deterioration of the electrode properties in general. Therefore a highly active catalyst for the heterogeneous decomposition of H_2O_2 (silver for instance) is required in the air electrodes. Another part of H_2O_2 may migrate through the electrolyte and its presence there even in small quantities, increases the self-discharge of the metal electrode (Zn, Fe). All these processes are very important for the operation of the air electrode and even for some metal-air system as a whole. Therefore, silver is used in air gas- diffusion electrodes either purely or cast on different carbon materials [12, 13]. Different studies [9, 14-17] report about the use of silver catalysts cast on materials with a high specific surface area, most commonly activated carbon, in alkaline electrolyte-operating gas-diffusion electrodes.

The purpose of this work is to investigate the catalytic activity of ultrasonic silver nanoparticles in air electrodes operating in a neutral electrolyte. Various methods of depositing silver nanoparticles on active carbon during the preparation of the catalytic layer of air electrodes are used. The polarization characteristics of the air electrodes have been investigated for 20 days. In order to confirm the catalytic ability of the silver particles obtained by ultrasound, the results are compared with those of an air electrode with activated carbon catalyst.

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EXPERIMENTAL

Silver nanoparticles synthesis methods

Silver nitrate ($AgNO_3$, Sigma-Aldrich), ethyl alcohol (96% C_2H_5OH, Valerus Co., Bulgaria) as a reducing agent and 25% aqueous ammonia solution (NH_4OH, Valerus Co., Bulgaria) were used to synthesize silver nanoparticles. A 6 mM silver nitrate solution was prepared using distilled water as solvent. The solution was mechanically stirred for about 10 minutes to complete dissolution of the silver nitrate by means of the magnetic stirrer with adjustable speed (Boeco MMS-3000). Without stopping the stirring, 0.8 ml of ethyl alcohol and 0.8 ml of ammonia solution were added one after the other to the solution. The total volume of the sample was 100 ml. The resulting mixture was placed in an ultrasonic bath model UST 2.8-100 (Siel Ltd., Gabrovo Bulgaria) with a power of 120 W for a period of about 5 minutes until a color change from colorless to deep yellow was detected. The temperature of the water in the ultrasonic bath was kept constant (50° C). The resulting samples were analyzed by a UV-Vis (T60 Uv-Visible spectrophotometer) and a transmission electron microscope (JEOL JEM 2100, 80-200 kV).

Gas-diffusion electrodes

The investigated gas-diffusion electrodes consist of a gas-supplying layer (100 mg/cm^2) and a catalytic layer (20 mg/cm^2 and 30 mg/cm^2). For the preparation of the gas-suplying layer, a hydrophobic material (carbon black P1042 and polytetrafluorethylene (PTFE)) was made using the procedure described in [18] and carbon paper. The used carbon paper is a commercial product known under the trade name (Freudenberg H2315) with carbon based microspores layer on one side. The thickness of the product was approximately 255μm, where the MPL (microspores layer) was only 50 to 55 μm. The through-plane ohmic resistance was 8 mΩ.cm^{-2} (by data from the provider) which made it suitable for gas diffusion media in secondary batteries.

Catalytic layers of active carbon (Norit NK-600 m^2/gspecific surface area) only are prepared as well as ones made using four different ways of applying silver nano particles on active carbon, namely:

- impregnation of active carbon with silver nanoparticle solution, 4% Ag;
- impregnation of active carbon with a solution of silver nanoparticles (4% Ag) and subsequent thermal treatment at 300 °C
- adsorption of silver nanoparticles on the active layer of the gas diffusion electrode, 5% Ag;
- adsorption of silver nanoparticles on one-sided hydrophobic carbon paper, 5% Ag.

Air electrodes of the same design and working area of 10 cm^2 were prepared from the samples. The electrochemical studies were performed by measurement of polarization curves under half-element conditions with an inert counter-electrode in 4 M NaCl at room temperature and working gas - air (for 20 days). Ag/AgCl was used as reference electrode.

RESULTS AND DISCUSSIONS

Characterization of Ag nanoparticles

On Fig. 1 a peak from UV-Vis spectrum is observed at a wavelength of about 420 nm, indicating the presence of spherical silver particles in the solution.

Further studies were carried out with a transmission electron microscope.

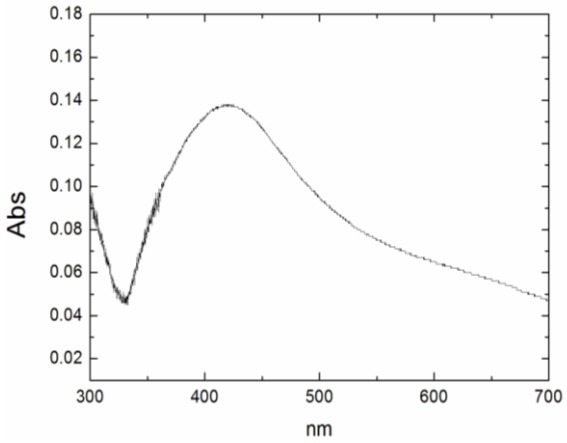

Fig. 1. UV-Vis spectrum of a colloidal solution containing silver nanoparticles

Fig. 2 (a) shows a general view of TEM sample at a magnification of 40, 000 times where separate evenly distributed particles are observed. There are also agglomerates. Increase 200,000 times (Fig. 2 (b)) the magnification of agglomerate it is seen that the dimensions of the individual particles are between 10 and 20 nm. The electron diffraction obtained via TEM is shown on Fig. 2. (c). The diffraction gives a description of the crystal structure of the silver nanoparticles. In this study it was found that it is hexagonal.

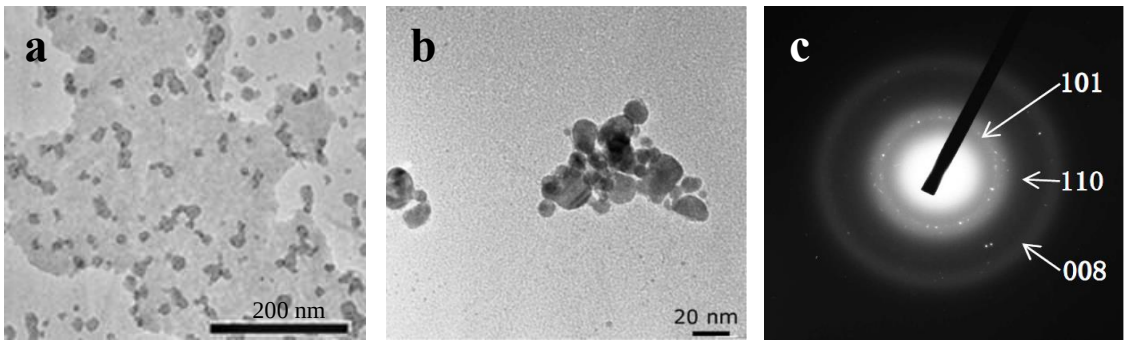

Fig. 2. TEM and diffraction images of silver nanoparticles synthesized using 6 mM aqueous solution of silver nitrate, ethanol and ammonia in an ultrasonic bath.

The XRD pattern of mixture of Norit NK – Ag nanoparticles is shown on Fig. 3. The broad peaks type "halo" at about 25.5 and 42.8 2θ are due to the amorphous carbon (Norit NK). The sharp peaks are related to the Ag particles. The low intensity of these peaks is due to the small amount (4%) of Ag nanoparticles. The comparison with PDF 04-0783 card proves the cubic structure of our nanoparticles. The particles with hexagonal structure are probably lower in compare with these with cubic structure, and by this reason, the XRD shows only these particles with cubic structure in the sample.

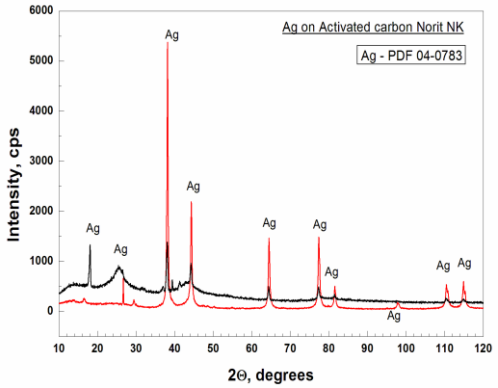

Fig. 3. XRD pattern of Norit NK – Ag nanoparticles mixture compared with cubic Ag standard

Application in gas-diffusion electrodes as catalyst

Fig. 4 shows the polarization characteristics of air electrodes with three types of catalysts: active carbon (Norit NK), the same active carbonactivated by silver nanoparticle solution and the last thermally treated after that at 300 °C.The electrodes have the same gas-supplying layers and equal active layer thickness made as a mixture of the respective catalyst and hydrophobic material at a ratio of 2:1. The amount of activating silver in the active layer of the electrodes is the same - 0.56 mg/cm^2. It is seen from the graphs that the introduction of a small amount of silver (4%) into the activated carbon improves the polarization characteristics of the electrodes. The gas-diffusion electrode with catalyst obtained by impregnating the active carbon with silver nanoparticle solution and subsequently thermally treated has better electrochemical characteristics thanother two electrodes especially at high current densities of over 50 mA /cm^2.

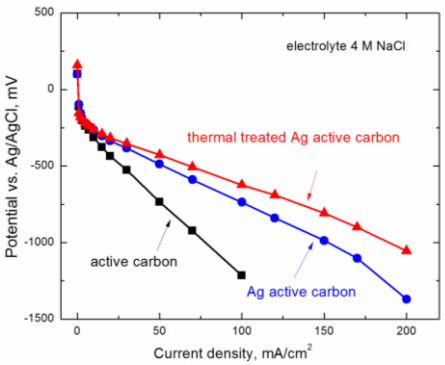

Fig. 4. Polarization curves of air electrodes with different catalysts, electrolyte 4 M NaCl

Ten polarization measurements were carried out on each of the electrodes under investigation during a period of 16 days. For this period the electrodes retain their working ability at a current density of 50 mA/cm^2, as shown on Fig. 5. This is more clearly seen in the electrode with a catalytic layer obtained by thermal treatment of the active carbon, impregnated with silver nanoparticle solution.

Fig. 6 shows polarization curves of air electrodes which have the same silver content (5%) in the catalytic layers. They differ in the gas-supplying layer and the way the silver nanoparticles have been applied. In one case, the silver nanoparticles are applied directly on the carbon paper, while in the other - on the active layer (Norit NK) of the gas-diffusion electrode.

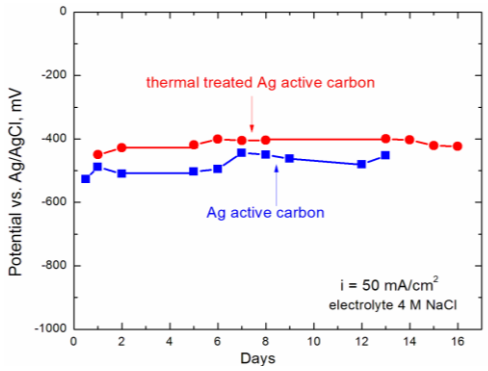

Fig. 5. Electrochemical behavior of the air electrodes at a current density of 50 mA/cm^2

The electrochemical reaction in the porous gas-diffusion layer is taking place on the active centers of the catalyst, located on the surface of the electrolyte-filled pores. The inclusion of silver nanoparticles by adsorption on active carbon results in a more uniform distribution of the catalyst over a large effective surface and an increase in its catalytic ability. It can be seen that when silver nanoparticles are deposited by adsorption on carbon paper, the polarization of the electrode is higher.

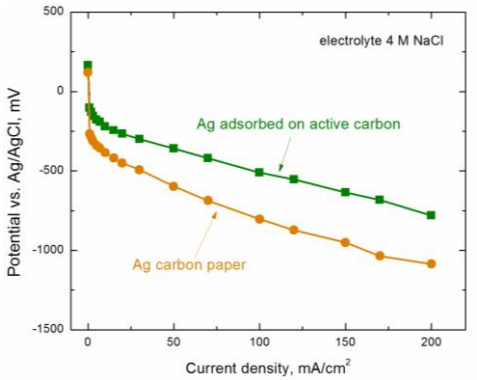

Fig. 6. Polarization characteristics of air electrodes with silver catalyst and various gas-supplying layers

One of the major transport processes in the air electrodes is the transfer of oxygen through the electrode's gas-supplying layer. Hindrances in this process are to a large degree determined by the properties of the porous structure of the gas-supplying layer. The difference in the polarizing dependencies of the two electrodes is due not only to the different ways of adsorption of silver nanoparticles, but also to the differences in the type of gas-supplying layers.

The transport hindrances of the oxygen through the various gas-supplying layers and the influence of the porous structure of a deposited catalyst are also reflected in the duration of the air gas-diffusion electrode operation. It is seen on Fig. 7 that during a period of 20 days, with 10 polarization characteristics carried out, the electrode with silver nanoparticles applied on active carbon remains stable at a current density of 50 mA/cm^2.

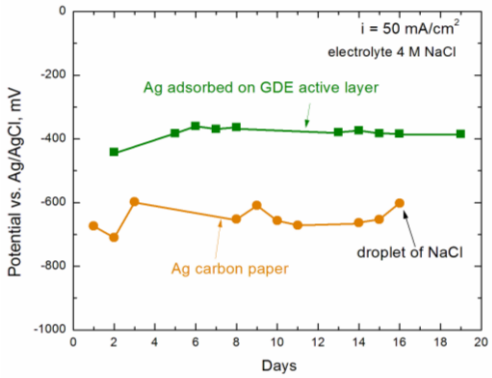

Fig. 7. Electrochemical behavior of air electrodes at 50 mA/cm^2

The electrode with adsorbed silver nanoparticles directly on carbon paper loses its hydrophobicity immediately after the tenth measurement. Disturbance of the hydrophobic properties leads to "electrolytic breakthrough" – passing of electrolyte through the electrode and leakage through its gas-supplying layer. This is most likely due to the large macro pores of the active layer, providing quick and easy electrolyte access to the carbon paper gas-diffusion layer.

CONCLUSION

The silver nanoparticles obtained by a new method are suitable for use as catalysts in gas-diffusion electrodes for Oxygen Reduction Reaction.

The good polarization characteristics of the electrodes, the small amount of activating silver used and the relatively easy preparation of the catalystsare a prerequisite for their future widespread application in different types of metal-air systems.

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НАНОРАЗМЕРНИ Ag ЧАСТИЦИ КАТО КАТАЛИЗАТОР В ГАЗОДИФУЗИОННИ ЕЛЕКТРОДИ ЗАРЕДУКЦИЯ НА КИСЛОРОД

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Постъпила на 11 септември, 2017 г.; приета на 29 ноември, 2017 г.

(Резюме)

Използван е оригинален метод за получаване на сребърни наноразмерни частици. Частиците са главно със сферична форма, като размерите им варират между 10 и 50 nm. Направената UV-Vis спектроскопия показва плазмен резонансен пик между 440 и 470 nm, което е индикация за наличие на сребърни наночастици. Изследването чрез трансмисионен електронен микроскоп показва, че имат хексагонална и кубична кристална структура.За да се потвърди каталитичната активност на получените сребърни наночастици, те са включени в активния слой на газодифузионни електроди. Активният слой на газодифузионните електроди е приготвен по четири начина. Каталитичната активност на тези електроди е изследвана в условията на полуелемент в електролит 4M NaCl и сравнителен електрод Ag/AgCl. Получените резултати показаха стабилна работа на всички електроди до 50 mA cm^{-2}, а на някой от тях до 100 mA cm^{-2}.

Ключови думи: Ag наноразмерни частици, Ag катализатор, въздушен газодифузионен електрод