Surfactant-free synthesis of carbon-supported silver (Ag/C) nanobars as an efficient electrocatalyst for alcohol tolerance and oxidation of sodium borohydride in alkaline medium

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Abstract

We have synthesized carbon-supported silver (Ag/C) nanobars by a simple surfactant-free hydrothermal method using glucose as the reducing reagent as well as the source of carbon in Ag/C nanobars. Physicochemical characterization of the materials was performed by X-ray Diffraction (XRD), field emission scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The XRD pattern confirmed the presence of a pure metallic silver phase. No carbon phase was detected, which indicates that the carbon exists mainly in the amorphous form. The electrocatalytic activity of Ag/C in different electrolyte solutions such as 0.5 M NaOH, 0.5 M NaOH + 1 M ethanol (EtOH), 0.5 M NaOH + 1 M ethylene glycol (EG), and 0.5 M NaOH + 0.01 M NaBH₄ (sodium borohydride) was studied by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronoamperometry (CA) study. Alcohol tolerance of the catalysts was also established in the presence of ethanol and ethylene glycol. The forward-to-backward current ratio from cyclic voltammetry (CV) study of Ag/C-20 (20 h) in 0.5 M NaOH + 1 M ethanol solution at 100 mV s⁻¹ scan rate is 4.13 times higher compared to that of Ag/C-5 (5 h). Hence, Ag/C-20 is a better candidate for the tolerance of ethanol. In the presence of ethylene glycol (1 M) in 0.5 M NaOH solution, it is obtained that the forward-to-backward current ratio at the same scan rate for Ag/C-20 is lower than that in the presence of ethanol. The durability of the catalyst was studied by chronoamperometry measurement. We studied the electrochemical kinetics of Ag/C catalysts for borohydride oxidation in an alkaline medium. The basic electrochemical results for borohydride oxidation show that Ag/C has very well strength and activity for direct borohydride oxidation in an alkaline medium. The reaction of borohydride oxidation with the contemporaneous BH₄⁻ hydrolysis was noticed at the oxidized silver surface. Among all the synthesized Ag/C catalysts, Ag/C-20 exhibited the best electrocatalytic performance for borohydride oxidation in an alkaline medium. The activation energy and the number of exchange electrons at Ag/C-20 electrode surface for borohydride electro-oxidation were estimated as 57.2 kJ mol⁻¹ and 2.27, respectively.

Keywords Carbon-supported silver (Ag/C) nanobars · Alcohol tolerance · Borohydride oxidation · Durability

1 Introduction

Over the last few decades, very expansive platinum (Pt) group metals were commonly used as electrocatalysts in energy devices due to their high conductivity and

less corrosion. But in the current century, researchers are searching for new cost-effective, stable, and efficient electrocatalysts to get much commercial success. Comparatively much low-priced materials such as nickel (Ni), cobalt (Co), copper (Cu), silver (Ag), and metal complexes can be

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used as electrocatalysts in the alkaline medium because of the extra advantage of these to be not so much corrosive [1]. During recent few years, researchers are showing their avid interest on borohydride fuel cell because the usage of liquid fuels in these cells gives good volumetric and gravimetric energy density [2, 3] and authorizes a bit of large theoretical open-circuit potential of 1.64 V [2, 4]. On the other hand, sodium borohydride (NaBH_4) has high hydrogen content (10.8 wt%), non-toxicity, low cost, and comparatively high stability in solution and solid states [5]. Fed with borohydride and alcohols like ethylene glycol or methanol in liquid fuels, it became an alternative of hydrogen in low-temperature fuel cells [6, 7]. Even though both direct methanol fuel cell (DMFC) and direct borohydride fuel cell (DBFC) can overcome the difficulty of hydrogen storage, DBFC is far better than DMFC in case of power performance, electrochemical activity, capacity value, and theoretical open-circuit voltage at a normal temperature [8]. The DBFC is considered an encouraging energy source because of its environmental friendliness, high cell voltage, and high energy density. Furthermore, the DBFC has a lower crossover problem than that of DMFC [9]. The optimum operating conditions for direct borohydride fuel cell were studied in different reported studies focusing on how the hydrolysis was carried out [10, 11].

At the anode, the borohydride oxidation kinetics in the presence of an alkaline medium take place according to the following reaction:

The process of complete eight-electron oxidation has a standard electrode potential of -1.24 V vs. SHE, which is 0.4 V more negative than that of methanol or hydrogen oxidation [2]. However, at electrolyte solutions having $\text{pH} < 12$ in the presence of some electrocatalysts, BH_4^- hydrolysis moves along with its oxidation [12]. The parallel action of this oxidation and hydrolysis generates H_2 and hydroxyborohydride ion (BH_3OH^-), and thereupon it reduces Coulombic efficiency [2]. In direct borohydride fuel cells (DBFCs), different electrolytes can be used with the presence of suitable catalysts and the most common is sodium borohydride (NaBH_4). The oxidation reaction of borohydride is given below:

From the overall borohydride oxidation reaction (Eq. 2), it is expected that the effective electron numbers have been reduced to less than 8.

It is already mentioned that platinum group metals and their alloys have colossal use as electrocatalysts for borohydride oxidation in energy devices like direct

borohydride fuel cells. To make cost-effective catalysts for fuel cells, non-platinum metals have been studied for borohydride oxidation. For commercial success, silver-based electrocatalysts have drawn much attention as silver is 60 times less cost and more abundant than platinum [13]. Besides all these, silver has high conductivity, high stability, and durability. Also, it has less corrosion and oxidation in moist air.

Different morphologies of silver including nanoparticles, nanowires, nanorods, nanodendrites, and nanocubes have been prepared with the help of numerous techniques. The 1D silver nanostructure being an apposite and important building block has nabbed much attention in material science research. It is quite hard to get 1D nanostructures of silver as silver is endowed with cubic crystalline symmetry. The most common technique to construct Ag nanowires is the template method [14, 15]. With the usage of PVP, Sun et al. synthesized the Ag/C nanocables under hydrothermal conditions [16]. Sun's group and Xia's group developed a solution-based technique to synthesize silver nanowires, showing that PVP has an important role in this nanostructure growth [17, 43]. With that, using the hydrothermal process Qian's group demonstrated an easy preparation method of silver nanowires [18]. A polymer-assisted preparation of core-shell Ag/C nanocables was exhibited by Wang et al. using the hydrothermal synthesis method [19]. The CTAB-assisted synthesis of carbon-supported silver nanostructures was also shown by Fang's group using hydrothermal conditions [20]. Synthesis of Ag/C nanocables with starch acts as a source of carbon, which was reported by Yu et al. [21]. In 2008, Jin et al. reported a synthesis technique of Ag/polymer/carbon nanocables using glucose as carbon precursors [22], although the growth mechanism is not completely clear till now. The 1D nanostructures of Ag/C have been developed so far with the help of some types of surfactant. In 2012, Mu et al. showed the surfactant-free synthesis of 1D carbon-supported silver nanostructure with a high aspect ratio in the presence of glucose, which plays the role of carbon source [23]. For energy device applications basically, catalysts have been prepared in a powder form and mixed with a conducting polymer solution to get the catalyst ink.

Supported metal electrocatalysts have wide use in energy devices because of the large influence of the supports on electrocatalytic activities [24]. Carbon has significant advantages like the high value of the specific surface area, long-term stability in basic and acidic media, trouble-free moderation of functional groups, and textural properties compared to other supports [25]. Therefore, a resurrection of interest has come out to synthesize a carbon-supported silver catalyst. In our work, we have followed the synthesis method of Mu et al. [23]. The

motivation of our work was the surfactant-free synthesis of 1D carbon-supported silver nanostructures using hydrothermal conditions and studies their electrochemical characterization for borohydride oxidation in alkaline solution for the promising application in alkaline borohydride fuel cells and alcohol tolerance. The conventional parameters, which express the electrochemical activity like the oxidation–reduction current density at certain potential, the charge transfer resistance, and the stability of electrode, were measured by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronoamperometry (CA) measurements, respectively. Stosevski et al. [1] synthesized Ag catalysts via a four-electron pathway for oxygen reduction and borohydride oxidation in an alkaline medium. They reported the value of activation energy in 2 M NaOH + 0.03 M NaBH₄ solution is 35 kJ mol^{−1}. In our work, we investigated the BOR kinetics of Ag/C having different structural morphologies, and among them, Ag/C nanobars showed better activity. We obtained better BOR kinetics of Ag/C catalysts in 0.5 M NaOH + 0.01 M NaBH₄ than that reported by Stosevski's group.

2 Experimental

2.1 Chemicals and reagents

All solutions for the experimental purpose were prepared using double distilled water. The metal precursors such as silver nitrate (AgNO₃), sodium sulfide (Na₂S), and glucose were purchased from Merck, India. All of these were analytical-grade reagents and used without further purification.

2.2 Synthesis of Ag/C catalysts

The catalysts were prepared by the hydrothermal method. The synthesis details were as follows: 1.18 mM of AgNO₃ was liquefied in 40 ml of double distilled water. Afterward, a 100 µl (1 M) aqueous solution of Na₂S was mixed with it. The mixed solution quickly became a black solution due to the formation of Ag₂S colloid. Then, the black solution was stirred for 15 min. 2.66 mM glucose was then added to that black solution under steady stirring. After 30 min of continuous stirring, the final solution was moved into a Teflon-linked stainless-steel autoclave (100 ml). The autoclave was made airtight and kept at 175 °C for different reaction times. After that, the sealed autoclave was cooled naturally to room temperature. We obtained a black precipitate of Ag/C nanobars. The precipitate was washed and filtered 10 times by double distilled water and ethanol, respectively, to remove the impurities. Finally, the product was dried at 65 °C in air and collected for the next characterizations. We prepared a set of samples with different

reaction times of 5 h, 10 h, 15 h, and 20 h and designated our samples as Ag/C-5, Ag/C-10, Ag/C-15, and Ag/C-20, respectively.

2.3 Structural characterizations of catalysts

The X-ray diffraction (XRD) patterns of all samples were recorded by an X-ray diffractometer (Proto AXRD) using CuKα radiation (1.54 Å) for 2θ in the range of 20°–80° with step size of 0.02°. To get XRD patterns, all samples were coated on different glass slides by drop-casting to make films, glass slides were cleaned by water, methanol, and acetone and next sonicated in double distilled water for 15 min in an ultrasonic cleaner before drop-casting on these.

The field emission scanning electron micrographs and EDX of the as-prepared samples were explored by ZEISS Gemini SEM microscopy.

2.4 Electrocatalytic measurements of catalysts

All the electrocatalytic measurements (cyclic voltammetry, electrochemical impedance spectroscopy, chronoamperometry) of as-prepared Ag/C samples were taken by a potentiostat/galvanostat (PGSTAT302N, Autolab, Metrohm). A platinum wire mesh and a 3.5 mol potassium chloride (KCl) saturated Ag/AgCl electrodes were employed as counter and the reference electrode, respectively. A glassy carbon electrode (GCE) having a 4 mm diameter was used as a working electrode in our work. The GCE was cleaned congruously by distilled water and ethanol all the time before each experiment. To make ready the catalyst ink, we used Nafion (Nafion™ NR 50, Merck) as a binder. 50 mg of Nafion has dissolved appositely in 40 ml ethanol, and then, 8 mg of Ag/C nanopowder was incorporated in the 1 ml of Nafion solution. The mixture was sonicated for 15 min in an ultrasonic vibrator to make the catalyst ink homogeneous. To modify the GCE surface, we drop-casted 12 µl catalyst ink and dried it for 2 h by a 100-W electric bulb. All the electrochemical measurements were taken at room temperature. The current densities in our work were calculated according to the geometric area (0.1256 cm²) of the working electrode.

3 Results and discussion

Characterization of Ag/C catalysts.

Scheme 1:

XRD analysis and Ag/C nanobar formation.

The phase purity and crystallinity of the synthesized Ag/C nanostructures were analyzed by the X-ray diffraction pattern. Figure 1 exhibits the XRD patterns of all Ag/C catalysts for preparation time of 5 h, 10 h, 15 h, and 20 h,

respectively. All the XRD peaks can be indexed by Miller indices (111), (200), (220), and (311), which indicate the fcc structure of Ag. No additional phase of silver oxide was observed from the XRD pattern, but very few less intense peaks of silver sulfide were observed. It is a clear indication that all the Ag species in our sample are cubic. No extra peaks for carbon were observed, which confirmed that the carbon in our Ag/C sample is in amorphous form. In reaction time of 5 h, the XRD peaks illustrated that the samples were mostly Ag; very few weak peaks for silver sulfide were observed. The position of diffraction peaks for Ag and Ag₂S can never be changed in later synthesis times up to 20 h. Insertion of sulfur ion reduces the rate of crystal formation by controlling the Ag⁺ ion concentration. In our experiment, the ratio of Ag⁺ ions to S²⁻ ions is nearly 5:1, although the XRD peaks of silver sulfide were extremely weaker, which confirmed that the silver sulfide colloid was reduced to metallic Ag in the presence of glucose. The intensity of XRD peaks of silver sulfide had not increased significantly in further increase of reaction times. In our synthesis technique, we guess that the growths of Ag/C nanobars were controlled by following ways: (i) low concentration of Ag⁺ ions controlled by silver sulfide which smooth the way for anisotropic development of silver nano-nuclei and (ii) coated layer of carbon further restricts the radial growth to form the 1D structure of Ag/C. The mechanism of Ag/C nanobars formation is as follows-

Fig. 1 XRD pattern of Ag/C for different synthesis times obtained at 175 °C temperature. **a** Ag/C-5, **b** Ag/C-10, **c** Ag/C-15, **d** Ag/C-20

Due to the presence of S²⁻ ions, the silver sulfide was produced with the following reaction:

Although the solubility of silver sulfide is excessively low, a small number of Ag⁺ ions were released by silver sulfide. According to reaction (3), a large number of Ag⁺ ion were consumed, but at the same time, the silver sulfide

In our experiment, Ag⁺ ions were reduced by glucose and allowed to leave a lot of H⁺ ions at the initial stage. It can be expressed by the following reaction:

broke into Ag^+ and S^{2-} ions following the equilibrium of reaction (4). Because of this, the content of silver sulfide in our product was reduced.

Subsequently, due to the coalesce of H^+ and S^{2-} ions generated from reactions (3) and (4), respectively, hydrogen sulfide (H_2S) was formed by following the reaction (5):

Being very sensitive to S^{2-} , the silver was eroded by hydrogen sulfide, which is expressed by the reaction given below.

Following the reaction (6), eroded silver was formed, and it released few Ag^+ ions. The reaction (6) was

controlled by silver sulfide, and this sluggish reaction is very helpful for the growth of 1D silver nanostructure. The silver sulfide of reaction (6) was reduced by glucose in our experiment, and the reaction stopped when the silver was layered by carbon. The reaction kinetics is given as:

Scheme 2: FESEM and EDX analysis

The morphology of the synthesized Ag/C powders was explored by the FESEM image. Figure 2a–d shows the FESEM images of all Ag/C catalysts. Figure 2 specifies that Ag/C-5 was mostly contained of particles and few spherical structures. Ag/C-10 was mainly contained in core/shell spherical structures. The dark inner core and outer layer are observed due to the presence of carbon and silver. It is found that Ag/C-15 composes few 1D structures with a light sheath layer and dark inner core along the axis. It is an indication that the 1D structure started to form. In higher reaction time, the number of 1D structure to the number of particles ratio was increased and the Ag/C-20 was composed of mostly 1D structure with an almost uniform diameter. We could notice that the 1D nanostructures have previously been shielded by a glassy layer. This identified that the formation of nanocables was led with the carbonization of glucose in the hydrothermal synthesis method. In the case of larger reaction time, we observed that the number of irregular particles reduced in our samples, and the product was largely composed of rod-like or bar-like 1D structures. EDX has been analyzed to explore the purity and compositions of synthesized samples. The EDX patterns of all samples are shown in the inset of their corresponding FESEM images. These patterns showed that the prepared Ag/C samples consist of carbon, oxygen, and silver. The silver content of Ag/C-5, Ag/C-10, Ag/C-15, and Ag/C-20 is 77.63, 42.3, 9.95, and 18.5 wt%, respectively.

Fig. 2 FESEM image of **a** Ag/C-5, **b** Ag/C-10, **c** Ag/C-15, **d** Ag/C-20. Their corresponding EDX patterns are given in the inset of FESEM images

Fig. 3 **a** CV of Ag/C-5 and Ag/C-20 at 0.5 M NaOH at 100 mV s^{-1} scan rate at 25°C , **b** CV of Ag/C-5 and Ag/C-20 at 0.5 M NaOH + 1 M EtOH at 100 mV s^{-1} scan rate at 25°C , **c** CV of Ag/C-20 at 0.5 M NaOH + 1 M EtOH and 0.5 M NaOH + 1 M EG at 100 mV s^{-1} scan rate at 25°C

3.1 Electrocatalytic performances of Ag/C

Firstly, we performed the cyclic voltammetry (CV) of our samples in 0.5M NaOH solution at a scan rate of 100 mV s^{-1} . Figure 3a displays the typical redox peaks for Ag/C-5 and Ag/C-20, which were associated with the oxidation and reduction of Ag, respectively. The oxidation peaks are due to the formation of silver oxide (Ag_2O), and the reduction peaks are associated with the reduction of Ag_2O to metallic silver [26, 27]. The Ag/C-5 sample has higher oxidation (forward) and reduction (backward) peak current than Ag/C-20 at almost the same potential vs. Ag/AgCl. Ag/C-5 has 0.092 mA cm^{-2} higher oxidation peak current and 2.44 mV negative sweep in the forwarding peak position than that of Ag/C-20. The CVs of these catalysts in the presence of alcohol were studied to establish their tolerance as an electrocatalyst in energy devices [26]. To study the activity of these catalysts for alcohol oxidation in an alkaline medium, CVs were done in 0.5M NaOH+1M EtOH solution and 0.5M NaOH+1M EG solution. Figure 3b shows the CVs of Ag/C-5 and Ag/C-20 in the presence of EtOH. The curves do not show alcohol oxidation behavior, indicating that Ag/C catalyst is not active for ethanol (EtOH) oxidation in alkaline media. At the same time, a blockage is observed of the peaks for the formation and reduction of silver oxide. This is the indication that ethanol is absorbed without oxidation [26]. The Ag/C-20 has shown a comparatively higher oxidation peak and 104.98 mV negative sweeps in

anodic peak in the presence of ethanol. The values of oxidation/forward current (J_f), reduction/backward current (J_b), and their peak positions vs. Ag/AgCl for Ag/C-5 and Ag/C-20 catalysts from Fig. 3a, b are presented in Table 1. The feature is the same in the presence of ethylene glycol (EG); the CV of Ag/C-20 in the presence of ethylene glycol is shown in Fig. 3c. It is clearly shown that Ag/C-20 has a lower anodic (forward) current in the presence of ethylene glycol than that of ethanol. The values of J_f , J_b and their peak positions for the Ag/C-20 catalyst from Fig. 3c are presented in Table 2. The forward-to-backward peak current ratio (J_f/J_b) roughly indicates the tolerance of catalyst surface to poisoning species from carbonaceous intermediates; a higher value of this ratio indicates a higher tolerance [28–33].

The high J_f/J_b values indicate the lower accumulation and effective removal of poisoning species on the electrode surface [34, 35]. That ratio is 4.13 times higher for Ag/C-20 than that of Ag/C-5 in the presence of ethanol, which is a good agreement with the CV profile in Fig. 3b; Ag/C-20 has a better activity of alcohol tolerance. The J_f/J_b value for Ag/C-20 in the presence of ethylene glycol is 2.73 times lower than that in the presence of ethanol. This is a clear indication that the Ag/C catalyst is more active for ethanol tolerance than that of ethylene glycol.

EIS is an important method to study electro-oxidation kinetics. It is a powerful tool to understand the properties of the interface of the modified electrode surfaces [36]. In

Table 1 Oxidation, reduction currents, and peak positions from Fig. 3a, b

Sample	Electrolyte							
	0.5 M NaOH				0.5 M NaOH + 1 M EtOH			
	Forward current J_f (mA cm^{-2})	Forward peak position (mV)	Backward current J_b (mA cm^{-2})	Backward position (mV)	Forward current J_f (mA cm^{-2})	Forward peak position (mV)	Backward current J_b (mA cm^{-2})	Backward position (mV) (J_f/J_b)
Ag/C-5	0.608	314.94 (Ag/AgCl) 1261.84 (RHE)	− 0.354	− 61.03 (Ag/AgCl) 885.87 (RHE)	0.116	268.55 (Ag/AgCl) 1209.55 (RHE)	− 0.153	− 131.83 (Ag/AgCl) 809.17 (RHE) − 0.75
Ag/C-20	0.516	317.38 (Ag/AgCl) 1264.28 (RHE)	− 0.218	− 56.15 (Ag/AgCl) 890.75 (RHE)	0.129	163.57 (Ag/AgCl) 1104.57 (RHE)	− 0.041	− 65.91 (Ag/AgCl) 875.09 (RHE) − 3.14

Table 2 Oxidation, reduction currents, and peak positions from Fig. 3c

Sample	Electrolyte				
	0.5 M NaOH + 1 M EG				
	Forward current J_f (mA cm^{-2})	Forward peak position (mV)	Backward current J_b (mA cm^{-2})	Backward position (mV)	(J_f/J_b)
Ag/C-20	0.115	249.02 (Ag/AgCl) 1195.92 (RHE)	− 0.100	− 156.25 (Ag/AgCl) 790.65 (RHE)	− 1.15

Fig. 4 **a** EIS at 0.5 M NaOH solution on Ag/C-5 and Ag/C-20 modified electrodes, **b** EIS at 0.5 M NaOH + 1 M EtOH on Ag/C-5 and Ag/C-20 modified electrode

Fig. 5 CA curves of Ag/C-5 and Ag/C-20 in 0.5 M NaOH solution at 0.3 V

our work, we carried on EIS between 10^5 and 0.1 Hz and at amplitude of 0.01V for all Ag/C catalysts at various electrolyte solutions. All the curves in our EIS profile display arc-like shapes. The diameter of the arc shapes in the EIS profile is an important parameter for measuring the electron transfer resistance (R_{ct}). The arc diameter is equal to R_{ct} [37]. The smaller diameter of the impedance arc indicates the lower value of R_{ct} for the electro-oxidation reaction that is the catalysts have good electron transfer kinetics and electrical conductivity for the electro-oxidation reaction, which is confirmable with good electrocatalytic activity [37]. Figure 4a, b displays EIS for Ag/C-5 and Ag/C-20 at 0.5M NaOH and 0.5M NaOH+1M EtOH solutions. In Fig. 4a, the arc diameter, i.e., R_{ct} , is smaller and in Fig. 4b that is higher for Ag/C-5 which is good agreement with the CVs profile in Fig. 3a, b, respectively.

The durability of electrocatalysts is an important thing for the electrochemical activity of those catalysts. Motivated from this, chronoamperometry (CA) for 1 hour was investigated to evaluate the stability of the catalysts. Figure 5 displays the CA curves of the Ag/C-5 and Ag/C-20 catalysts in 0.5M NaOH solution at 0.3V (vs. Ag/AgCl). In the first phase, it is observed that the catalysts showed a rapid current decay because of the absorbance of species

Fig. 6 CV of Ag/C-20 at 0.5 M NaOH + 0.01 M NaBH₄ at different scan rates at 25 °C. Corresponding plot of maximum forward peak currents versus square root of scan rates for all Ag/C catalysts are shown in inset

on the electrode diffusion layer, and after that, it followed constant current up to the complete study of 1 hour [38, 39]. The constant current with time signifies the stability of catalysts [34]. From this CA study, it is clear that Ag/C-5 has lower current decay than that of Ag/C-20 at 60 min. That indicates in 0.5M NaOH solution Ag/C-5 has higher durability than that of Ag/C-20, which is good assistance of CV and EIS profile in the same solution.

To understand the borohydride oxidation (BOR) kinetics of the Ag/C electrode, we investigated the cyclic voltammetry of all Ag/C electrodes in the presence of NaBH₄ at different scan rates. The typical cyclic voltammetry of the Ag/C-20 electrode is shown in Fig. 6 with different scan rates in a 0.5M NaOH+0.01M NaBH₄ solution. The electrocatalytic behavior for borohydride oxidation is complicated because of more than one oxidation peak. In forward scan, a large oxidation peak is observed at around 0.2V (vs Ag/AgCl), followed by another anodic peak having a broad hump but a small height at around 0.6V (vs Ag/AgCl). During the backward scan, we observed a well-defined anodic spike at around 0.65V (vs Ag/AgCl). The first peak at around 0.2V (vs Ag/AgCl) is due to H₂ oxidation, which is produced

Fig. 7 CV of all Ag/C at 0.5 M NaOH + 0.01 M NaBH₄ at 100 mV.s⁻¹ scan rate at 25 °C

by BH₄⁻ hydrolysis, and the second peak at around 0.6V (vs Ag/AgCl) in the forward scan is observed because of the direct BH₄⁻ oxidation on Ag/C electrocatalyst with BO₂⁻ and hydrogen as products [8].

The current is still in increasing fashion after direct BH₄⁻ oxidation with the formation of silver oxide, which is the direct borohydride oxidation that mainly happened upon multilayered silver oxide [40].

The peak at around 0.65V (vs Ag/AgCl) in a backward scan corresponds to the oxidation of BH₃OH⁻ or the surface-adsorbed intermediates of BH₃OH⁻ on the catalyst surface, which is partially oxidized [1, 2].

With the increase of scan rates of cyclic voltammetry (Fig. 6), it is clear that the maximum oxidation peak potentials in the forwarding scan showed a positive shift followed by the increment in the current. This positive shift of maximum forward peak potentials with the scan rates is a feature of irreversible systems [41–43]. Figure 7 displays the CV profile of all the synthesized Ag/C catalysts in the same solution. Among all the catalysts, Ag/C-20 showed the maximum forward peak current of 4.38 mA.cm⁻² at 202mV (vs Ag/AgCl) potential. The obtained value of

Table 3 Forward peak currents and corresponding peak potentials from Fig. 7

Electrocatalyst	Forward peak current (mA cm ⁻²)	Forward peak potential (mV)
Ag/C-5	0.36	39 (Ag/AgCl) 1021.3 (RHE)
Ag/C-10	1.26	207 (Ag/AgCl) 1189.3 (RHE)
Ag/C-15	0.94	68 (Ag/AgCl) 1050.3 (RHE)
Ag/C-20	4.38	202 (Ag/AgCl) 1184.3 (RHE)

Fig. 8 EIS at 0.5 M NaOH + 0.01 M NaBH₄ solution on all Ag/C modified electrodes. Inset shows the EIS profile of Ag/C-20 up to very low frequency

Fig. 9 CA curves of all Ag/C catalysts in 0.5 M NaOH + 0.01 M NaBH₄ solution at 0.2 V. Inset shows the chronoamperometry profile of Ag/C-20 up to 1 h

forwarding peak current is higher than that reported by Stosevski et al for Ag/C catalysts [1] in 2M NaOH + 0.03M NaBH₄ electrolyte solution at 50 mV.s⁻¹ scan rate. The value of maximum forward currents and corresponding potentials is listed in Table 3. Inset of Fig. 6 displays the graph of

forwarding peak current versus square root of scan rate of all active catalysts. We observed an almost linear relationship between the square root of scan rate and forward peak current. These results indicate that the borohydride oxidation on Ag/C modified electrode surface is probably the diffusion-controlled process; the largest slope value of these graphs suggested the good electro-oxidation and electron transfer kinetics of Ag/C-20 [43, 44].

Figures 8 and 9 are the EIS and chronoamperometry representation at 0.5M NaOH+0.01M NaBH₄ solution at all Ag/C modified electrodes. The high-frequency portion of the EIS profile is a semicircular impedance arc, the diameter of which corresponds to faradic electron transfer resistance at the electrolyte–electrode interface during borohydride oxidation. The EIS profile showed the lowest arc diameter for Ag/C-20, confirming its highest electrochemical kinetics for borohydride oxidation. In the inset of the EIS curve, the low-frequency part of the Ag/C-20 electrode shows an almost linear nature. The semicircular impedance arc and the linear portion of this EIS profile confirm the charge-transfer-limited process and diffusion-limited process, respectively [30]. Chronoamperometry of all Ag/C catalysts has done in 0.5M NaOH+0.01M NaBH₄ solution at 0.2V to verify the stability of the electrodes in that electrolyte. We observed a rapid current decay initially in 1 second followed by a fixed value of current till the complete study. The rapid current decay in the first phase is due to the absorbance of species on the electrode diffusion layer. The constant value of current with time indicates that Ag/C is a stable candidate as an electrocatalyst for borohydride oxidation in alkaline medium. From this chronoamperometry study, it is confirmed that Ag/C-20 has the lowest current decay than other Ag/C catalysts indicating its better electrochemical kinetics for borohydride oxidation. Inset of chronoamperometry profile shows the good stability of Ag/C-20 catalyst up to 1 hour.

Fig. 10 CV curves of Ag/C-20 at different temperatures at 0.2 V in 0.5 M NaOH + 0.01 M NaBH₄. Inset shows the corresponding plot of log *j* vs 1/*T*

The apparent activation energy (*E*_{app}) for the borohydride oxidation reaction at Ag/C-20 electrodes in 0.5M NaOH + 0.01M NaBH₄ electrolyte solution was measured from CA data (Fig. 10) in the 25–60 °C temperatures range, using the Arrhenius equation (Eq. 13):

$$\frac{\partial \log j}{\partial T} = -\frac{E_{\text{app}}}{RT^2} \quad (13)$$

where *j* is the current density (mA cm⁻²), *T* is the thermodynamic temperature (K) and *R* is the molar gas constant (8.314 J mol⁻¹ K⁻¹). The CA data at different temperatures indicate that the electrocatalytic performance of NaBH₄ was improved by increasing the temperature, which proves that electrode reaction dynamics become faster at higher temperatures. Inset of Fig. 10 presents the Arrhenius plot of log *j* versus 1/*T*. From the slope of this plot and using the Arrhenius equation (Eq. 13), the value of *E*_{app} of Ag/C-20 for BOR was estimated as 57.2 kJ mol⁻¹, which is higher in comparison with previous reports. The value of *E*_{app} for borohydride oxidation reaction at several electrocatalysts, such as CoBi, Pt/C, Pt_{0.75}Ni_{0.25}, and Pt_{0.75}Co_{0.25}, is 36.774, 34.3, 20.2, and 25.3 kJ mol⁻¹, respectively [4, 45]. For Ag electrode, the already reported value is 35 kJ mol⁻¹ [1].

Cottrell equation was used to calculate exchanged electron number (*n*) during borohydride electro-oxidation of Ag/C-20 catalyst as given below:

$$j = \frac{nFC(D)^{1/2}}{(\pi t)^{1/2}} \quad (14)$$

where *F* is the Faraday constant (96485 C mol⁻¹), *C* is the BH₄⁻ concentration and *D* is the diffusion coefficient. Wang and co-workers [46] reported values of *D* for BH₄⁻ oxidation at different temperatures in different concentrations of NaOH, assuming that *D* does not depend on BH₄⁻ concentration. Using the value of *F*, *C*, and from the slope (slope value = 5.229) of *j* versus *t*^{-1/2} plots, *n* value for BH₄⁻ electro-oxidation at Ag/C-20 electrode in 0.5M NaOH+0.01M NaBH₄ at 30 °C was found to be 2.27, which is comparable to the reported values for BOR at Pt_{0.4}Dy_{0.6} and Pt_{0.5}Dy_{0.5} electrodes (2.5 and 2.4, respectively) at 25 °C [2]. Value of exchanged electrons lower than 8 indicates partial anodic oxidation of BH₄⁻, with loss of available electrons due to BH₄⁻ hydrolysis.

To study the effect of NaBH₄ concentration on electrocatalytic performance of Ag/C catalyst for borohydride oxidation, CV in different concentrations of NaBH₄ (0.005M, 0.01M, 0.015M, 0.02M, 0.025M and 0.03M) was investigated at Ag/C-20 electrode. Figure 11 displays the CV profile of Ag/C-20 in different concentrations of NaBH₄. It was clear from the CV profile that increment of NaBH₄ concentration resulted in the significant enhancement

Fig. 11 CV of Ag/C-20 in 0.5 M NaOH + x M NaBH₄ at 70 mV.s⁻¹ scan rate and 25 °C temperature. Inset shows the corresponding plot of log *j* vs log [NaBH₄ concentration]

of forwarding current densities, indicating a strong electrocatalytic property of Ag/C nanobars toward borohydride electro-oxidation. The forward current densities and corresponding peak positions are given in Table 4. We observed a remarkable enhancement of current up to 0.025M increment of NaBH₄. But a decrease of current for further increase of NaBH₄ (0.03M) was observed. This is because of the continuous consumption of NaBH₄ on the electrode surface at a very high concentration of NaBH₄ after 0.025M. That can perturb the electrochemical kinetics of investigated electrode. Also, we noticed a positive shift of peak potentials at higher NaBH₄ concentration.

To determine the order of reaction, we used the following equation [40]:

$$i = zC^\beta \quad (15)$$

where *z* is a constant, *i* and *C* are the peak current and NaBH₄ concentration, respectively, and β is the order of the

reaction. The slope value of log *j* vs log [NaBH₄ concentration] obtained from Fig. 11 defines the order of the reaction. The value of this slope of this plot is 0.80, which indicates that the borohydride oxidation in the Ag/C electrode is a first-order reaction. Borohydride electro-oxidation in different materials like PtDy was also reported to be first order [2].

3.2 Conclusion

Ag/C nanostructures were synthesized hydrothermally in different reaction times of 5 h, 10 h, 15 h, and 20 h using glucose as a reducing agent and carbon source. Cyclic voltammetry for Ag/C was studied in several electrolytes. Ag/C-5 showed better electrochemical activity in alkaline solution than Ag/C-20, but it has less alcohol tolerance than that of Ag/C-20, which suggests that Ag/C 1D nanostructure has a comparably higher tolerance of poisonous species. All Ag/C catalysts were investigated for borohydride electro-oxidation reaction in an alkaline medium for prospective application as an electrocatalyst in alkaline direct borohydride fuel cell (DBFC). All Ag/C catalysts exhibited sharp anodic current for borohydride electro-oxidation. Borohydride oxidation reaction at carbon-supported silver electrocatalysts is accepted to be happened due to the generation of surface oxides of silver. Chronoamperometry study displayed constant current after a rapid decay in the 1st second, which implies the stability of Ag/C as a potential electrocatalyst. Ag/C nanobars showed better performance as an electrocatalyst for BOR in an alkaline medium than other synthesized Ag/C. Thus, being affordable and stable carbon-supported silver nanobar can be used as a propitious anode in the borohydride fuel cell.

Table 4 Forward peak current densities and corresponding peak potentials from Fig. 11

Electrolyte solution	NaBH ₄ concentrations (x M)	Forward peak current (mA cm ⁻²)	Forward peak potential (V)
0.5 M NaOH + x M NaBH ₄ (x = 0.005, 0.01, 0.015, 0.02, 0.025, 0.03)	0.005	2.777	0.063 (Ag/AgCl) 1.045 (RHE)
	0.010	3.495	0.051 (Ag/AgCl) 1.033 (RHE)
	0.015	5.152	0.065 (Ag/AgCl) 1.047 (RHE)
	0.020	8.085	0.109 (Ag/AgCl) 1.085 (RHE)
	0.025	9.705	0.202 (Ag/AgCl) 1.178 (RHE)
	0.030	8.160	0.205 (Ag/AgCl) 1.181 (RHE)

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Declaration

Conflict of interest There is no conflict of interest.

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