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Silver–carbon electrocatalyst for air cathodes in alkaline fuel cells

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Abstract

A method for producing electrocatalysts containing silver supported on different carbons was developed. The catalysts were investigated in air (oxygen) diffusion electrodes in alkaline electrolyte (7 M KOH). Depending on the carbon support used, up to a threefold improvement in electrode performance was achieved compared with the activity of the uncatalysed carbon in this media. At ambient temperature and atmospheric pressure, a current density of 150 mA/cm^{-2} was obtained at electrode potential 1.2 V vs zinc (0.75 vs HE). A correlation between electro catalytic activity and wetted surface area of the electrocatalysts was found.

1. Introduction

Alkaline fuel cells (AFCs) show promise as environmentally friendly electrochemical power sources for electromotive, stationary and portable applications. Compared to the more recently developed proton exchange membrane (or polymer electrolyte membrane, PEMFC) and direct methanol fuel cell (DMFC), AFC possess at least two significant advantages. These are the use of much less costly electrolyte and the potential use of non-platinum electrocatalysts at the air (oxygen) cathode without loss of performance. The most active non-platinum catalysts for alkaline air cathodes are pyrolyzed metal chelates such as substituted tetra phenyl porphyrins (TPP) and tetraazaannulenes (TAA) of Co and Fe [1, 2]. Air electrodes with these catalysts operate several thousand hours with negligible loss of performance at ambient temperature. However, exposure to typical AFC operating temperatures (60–80 °C) results in rapid performance loss over tens of hours caused by loss of stability of pyrolyzed metal chelates [3]. One means of overcoming such performance failure is via electrocatalyst stabilization by additives acting as protectors. Alternatively, a more stable electrocatalyst offering high current density in alkaline electrolyte at elevated temperature may be used. Silver is an active electrocatalyst for oxygen reduction under these conditions [4] and is an excellent catalyst for the heterogeneous decomposition of hydrogen peroxide [5]. Moreover, highly-dispersed silver/PTFE-based electrodes give stable operation as oxygen cathodes in chlorine-alkali cells under extremely high current density conditions [6, 7].

The aim of this work was to develop a method for producing of silver supported on carbon electrocatalyst for air cathodes and to evaluate their initial performance for use the AFC. Several types of high-surface carbons with different structures and surface areas were used as catalyst supports. Special attention was paid on the influence of the supports on overall electrocatalyst performance.

2. Experimental details

2.1. *Preparation of catalysts and fabrication of gas diffusion electrodes*

Electrocatalyst preparation was based on deposition of silver on high-surface-area carbon [8, 9] followed by heat treatment under a flow of inert gas. Four types of carbon, listed in Table 1, were used as a support. The carbons (4.0 g) were added to a solution containing 0.317 g of silver nitrate ($AgNO_3$) in 50 ml of distilled water. After stirring for 30 minutes, the water was removed from the suspension by evaporation and drying. The silver nitrate/carbon compounds were heated in stream of argon for one hour at 700 °C. During this procedure the following reactions take place:

$$AgNO_3 \longrightarrow AgO + NO_2 \tag{A}$$

$$AgO + C \longrightarrow Ag + CO \tag{B}$$

Standardized double-layer electrodes (active plus gas-diffusion layers) were prepared by pressing at 300 kg cm^{-2} at ambient temperature. The gas diffusion layers contained 0.05 g cm^{-2} teflonized (35 wt %

Table 1. Characteristics of raw carbon materials

Brand name	Source	Type	Code in text	BET area/m^2 g^{-1}
Norit SA-3	Aldrich	Activated carbon	SA-3	650
Vulcan XC-72	Cabot	Furnace black	VCB	254
Shawinigan Black	Chevron	Acetylene black	SAB	70
Graphite 287	Johnson Matthey	Powdered graphite	JMGR	33

PTFE) acetylene black. The active electrocatalytic layers contained different amounts of supported silver electrocatalyst mixed in different ratios with teflonized acetylene black. The optimal composition of these active layers is shown in Table 2. Nickel screens with 0.15 mm diameter wires were embedded into the gas diffusion layers as a current collectors.

2.2. *Electrochemical measurements*

Steady-state polarization behaviour of 5 cm^2 electrodes fed by pure oxygen and air at atmospheric pressure was examined in a half-cell at ambient temperature in 7 M KOH. A zinc wire placed close to the active layer was used as a reference electrode and nickel mesh was used as a counter electrode [10, 11].

During the heat treatment of $AgNO_3/C$ compounds, partial surface oxidation of carbon supports due to reactions A and B and some increase in the hydrophilic properties of the obtained catalysts could be expected. By this reason the evaluation of wetted area of the catalysts was carried out using the charging curve method developed by Frumkin and Shlygin [12]. This uses charge/discharge of the double layer capacity (C_{DL}) by cathodic and anodic polarization at sufficiently low current ($I_{c/d}$) in the absence of Faradaic processes. The change of electrode potential with the time was recorded and the average slope of the linear part of the potential–time curves (dE/dt) was determined. The double layer capacity C_{DL}, wetted surface area of catalyst in F g^{-1} was calculated using

$$C_{DL} = \frac{I_{c/d}}{M_{CAT}} \times \left(\frac{dt}{dE}\right) \qquad (1)$$

where M_{CAT} is the mass of silver/carbon catalyst in the electrode.

The charging curves of all raw carbons and catalysts were carried out in the same cell after the polarization measurements of gas diffusion electrodes.

Table 2. Composition of active layers of electrodes

Code	Active layer /g cm^{-2}	Catalyst Ag/C /g cm^{-2}	Silver /g cm^{-2}
SA-3	0.01	0.075	3.75×10^{-4}
VCB	0.005	0.0025	1.25×10^{-4}
SAB	0.005	0.003	1.5×10^{-4}
JMGR	0.005	0.0033	1.65×10^{-4}

3. Results

3.1. *Polarization characteristics of gas diffusion cathodes*

Initial polarization curves for air cathodes with different Ag/C catalysts are compared with those for the carbons alone in Figures 1–4. The results show that in all four cases the silver deposit improves cathode performance. However, the improvement is minimal with SA-3 support (Figure 1, see codes in Table 1) and is greatest with VCB (Figure 2). To find how much the overall performance depends on increased electrochemical activity and/or decreased mass transport resistance within the porous electrocatalyst structure, a simple method [13] based on a separate analysis of electrode perfor-

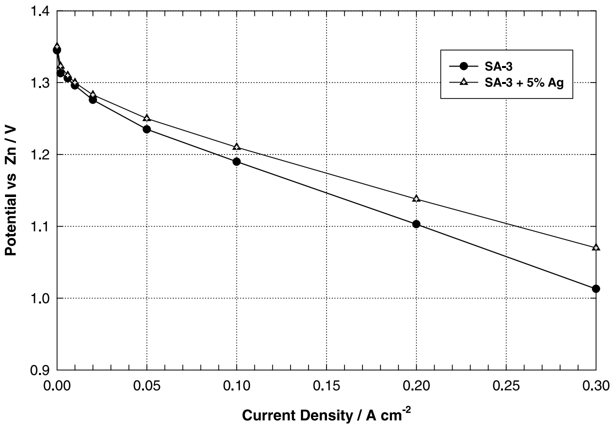

Fig. 1. Polarization curves for air cathodes, SA-3 and Ag/SA-3 electrocatalysts.

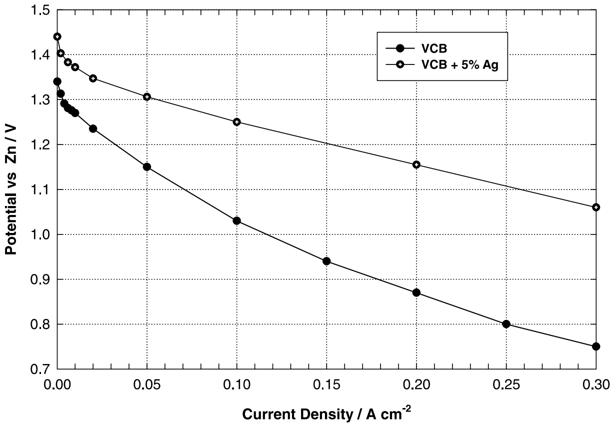

Fig. 2. As Figure 1, VCB and Ag/VCB electrocatalysts.

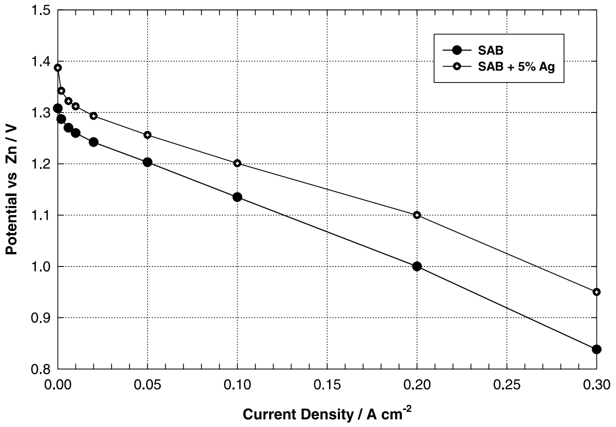

Fig. 3. As Figure 1, SAB and Ag/SAB electrocatalysts.

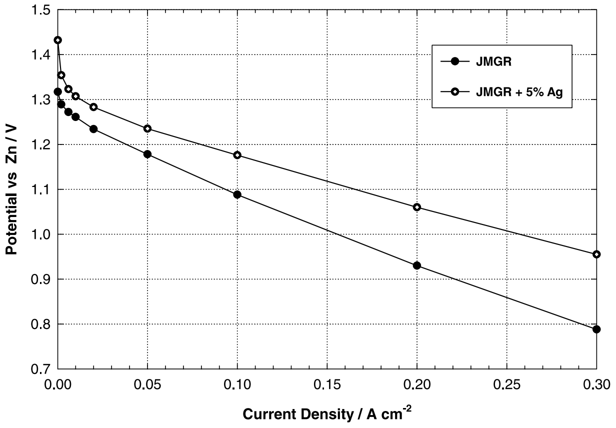

Fig. 4. As Figure 1, JMGR and Ag/JMGR electrocatalysts.

mance under kinetic and mass transport control was used. This is illustrated in Figure 5–7 for electrodes with SAB carbon alone and Ag/SAB. These show Tafel plots (Figure 5), polarization curves under pure oxygen (Figure 6) and $\Delta E/i$ plots (Figure 7), where ΔE is the potential difference between electrode operation under pure oxygen (E_{oxy}) and air (E_{air}), taken from polarization curves for each value of current density.

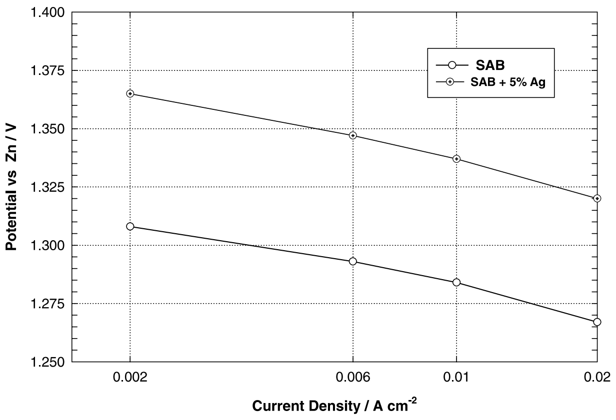

Fig. 5. Tafel plots for oxygen cathodes, SAB and Ag/SAB electrocatalysts.

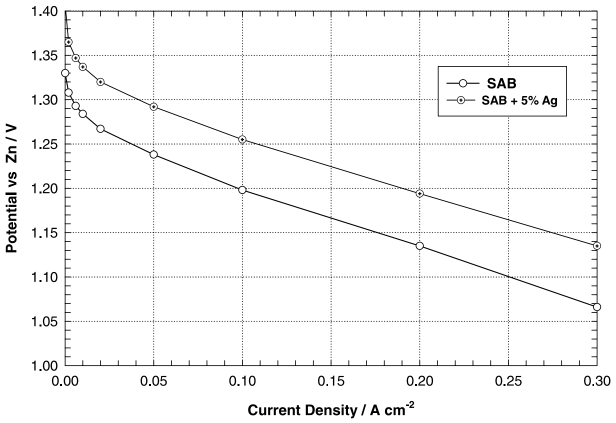

Fig. 6. Polarization curves of oxygen cathodes, SAB and Ag/SAB electrocatalysts.

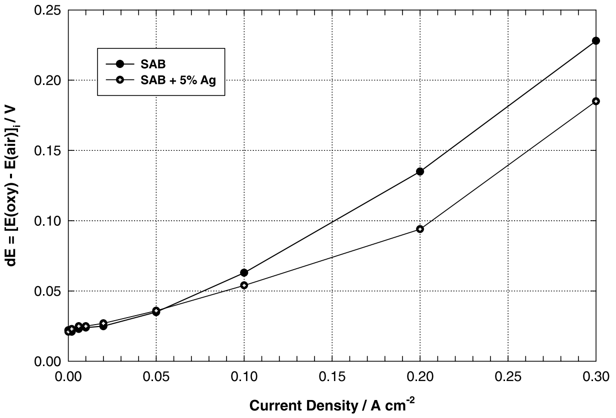

Fig. 7. Potential difference against current density plots for air and oxygen cathodes, SAB and Ag/SAB catalysts.

To evaluate electrocatalyst activity, the electrode potential at 0.006 A cm^{-2} under pure oxygen (E_{oxy} at 0.006 A cm^{-2}) was determined from the linear sections of the Tafel plots in Figure 5. Under these condition, mass transport resistances within the porous cathode structures are negligible. The slope of linear part of the polarization curve under pure oxygen $(\Delta E/\Delta i)_{\mathrm{oxy}}$ in Figure 6 is proportional to the ionic resistance of the electrolyte in the hydrophilic pores of the active layer. The potential difference $\Delta E_{0.2}$ between operation on pure oxygen and air at a sufficiently high current density (0.2 A cm^{-2}) from Figure 7 characterizes gas diffusion hindrances into hydrophobic gas-filled pores. These values are summarized in Table 3 for all electrodes.

3.2. *Wetted area of catalysts*

Potential–time, i.e., charging, curves at constant current carried out in argon atmosphere for all measured gas diffusion electrodes. From the slopes $(\Delta E/\Delta t)$ of the linear parts of charging curves (between 0.6–0.9 V), double layer capacities C_{DL} were calculated using Equation 1. C_{DL} for all the raw carbons and electrocatalysts was determined in this manner, and results are shown in Table 4.

Table 3. Electrochemical activities, ionic resistance and transport hindrance in air electrodes

Raw carbon /catalyst	E_{oxy} (at 0.006 A cm^{-2})/V	$(dE/dI)_{\text{oxy}}$ /Ω cm^2	ΔE at 0.2 A cm^{-2} /V
SA-3	1.306	0.056	0.061
Ag/SA-3	1.334	0.036	0.056
VCB	1.312	0.116	0.164
Ag/VCB	1.414	0.067	0.080
SAB	1.293	0.066	0.135
Ag/SAB	1.347	0.060	0.094
JMGR	1.296	0.103	0.140
Ag/JMGR	1.368	0.062	0.120

Table 4. Double layer capacities of raw carbons and Ag/C catalysts

Code	DL capacitance/F g^{-1}
SA-3	85
Ag/SA-3	100
VCB	88
Ag/VCB	121
SAB	40
Ag/SAB	64
JMGR	70
Ag/JMGR	75

3.3. *Hydrophilic properties and overall activity of catalysts*

The obtained data summarized in Table 3 show that the introduction of silver onto or into the carbons affects all components of overall activity, the largest effect being on $(\Delta E/\Delta i)_{\text{oxy}}$, the ionic resistance of the electrolyte in the hydrophilic pores. The introduction of silver increases the hydrophilic properties of catalysts, probably because of partial surface oxidation of carbons during the preparation of catalyst. This effect is demonstrated by the results for wetted area of catalysts, measured as double layer capacity. As it can see from Table 4, in all cases the wetted area of Ag/C catalysts increases, compared with wetted area of raw carbons. The wetted area of catalysts (silver and carbon) correlates well with their electrochemical activity E_{oxy} (at 0.006 V) as it is shown in Figure 8.

4. Discussion

One of the most important characteristics of electrocatalysts for air (or oxygen) cathodes must be their long term stability at high current density and elevated temperature (60–90 °C). Under these conditions, only carbon-supported platinum [14, 15], gold-supported platinum [16] and unsupported, highly-dispersed silver [6] appear to show sufficient stability. The more important reasons for the instability of other carbon-supported electrocatalysts is the destruction of active electro catalytic centres and corrosion of the carbon support by the hydroperoxide (HO_2^-) anion, an intermediate in oxygen reduction in alkaline electrolyte. To achieve long-term stability, stable carbon supports combined with highly active and stable electrocatalyst is required. Silver is stable under operating conditions of AFC (pH > 14, potential range 0.5–1.0 V vs RHE) [17]. There is some evidences for slight corrosion of silver as silver oxide in strong alkaline solution [18], but this process takes place at potentials, higher that 1.05 V.

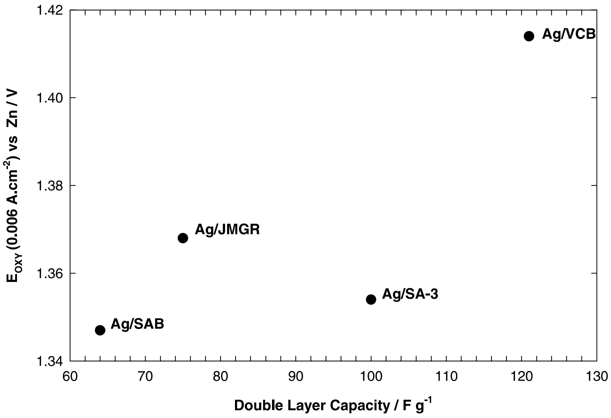

Fig. 8. Correlation between electrochemical activity and wetted surface area, Ag/C electrocatalysts in air cathodes.

Three types of carbon powders (activated carbon, carbon black and graphite) were studied in this work to determine maximum initial performance. The results show the highest performance is that for Ag/VCB electrocatalyst, but it is not known how stable this carbon support will be under real AFC operating condition. However, graphite is most stable carbon in respect to oxidative corrosion. In spite of the lower initial performance of electrodes with Ag/JMGR electrocatalyst, it appears reasonable that effort on improving its catalytic activity associated with accelerated long-term stability test under AFC operating conditions will be useful.

5. Conclusions

Conclusions are as follows:

(i) A simple method for the preparation of carbon-supported silver air or oxygen cathode electrocatalysts for the AFC was developed.
(ii) The influence of the carbon support on overall cathode performance was studied.
(iii) It was shown that introduction of silver onto or into carbon increases the hydrophilic properties of the electrocatalysts.
(iv) To achieve acceptable long-term air cathode stability, further work will concentrate on Ag/JMGR electrocatalyst.

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