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ORIGINAL PAPER

# Studies of some operating parameters and cyclic voltammetry for a direct ethanol fuel cell

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**Abstract** A direct ethanol fuel cell (DEFC) of 5 $cm^2$ membrane-electrode area was studied systematically by varying the catalyst loading, ethanol concentration, temperature and different Pt based electro-catalysts (Pt–Ru/C, Pt-black High Surface Area (HSA) and Pt/C). A combination of 2 M ethanol at the anode, pure oxygen at the cathode, 1 mg $cm^{-2}$ of Pt–Ru/C (40%:20%) as the anode and 1 mg $cm^{-2}$ of Pt-black as the cathode gave a maximum open circuit voltage (OCV) of 0.815 V, a short circuit current density of 27.90 mA $cm^{-2}$ and a power density of 10.3 mW $cm^{-2}$. The optimum temperatures of the anode and cathode were determined as 90 °C and 60 °C, respectively. The power density increased with increase in ethanol concentration and catalyst loading at the anode and cathode. However, the power density decreased slightly beyond 2 M ethanol concentration and 1 mg $cm^{-2}$ catalyst loading at the anode and cathode. These results were validated using cyclic voltammetry at single electrodes under similar conditions to those of the DEFC.

**Keywords** Direct ethanol fuel cell (DEFC) · Ethanol · Pt electrode catalyst · Cyclic voltammetry

## 1 Introduction

During the last decade the electrochemical oxidation of alcohols, especially methanol, in direct methanol fuel cells (DMFC), has been widely investigated [1, 2]. Recently, it has been shown that ethanol is both more convenient and efficient compared to methanol and other higher alcohols. The low boiling point and toxicity of methanol and its status of not being a primary fuel has led investigators to shift focus from methanol to ethanol, which is less toxic and less volatile than methanol. Ethanol can be produced in large quantity by fermentation of sugar-containing biomass resources and is thus renewable in nature. All these advantages favour ethanol as fuel for direct ethanol fuel cells (DEFC) [1].

The electrocatalytic oxidation of ethanol has been investigated at different platinum based electrodes, e.g., Pt–X alloys (with X = Ru, Sn, Mo) by Lamy et al. [3]. Among these, Pt–Ru and Pt–Sn were the most effective electrocatalysts for DEFC. The electrooxidation of ethanol is more difficult than that of methanol since it is necessary to break the C–C bond for complete oxidation. A review of the infrared reflectance spectroscopy and gas chromatography experimental data shows that electrooxidation of ethanol leads to the formation of intermediate products with C–C bonds and adsorbed CO poisoning species [3]. Lamy et al. [4, 5] analysed the detailed electrooxidation reaction mechanism of ethanol and the catalyst role (bi-functional mechanism of Pt–Ru/C) in anode reactions. Recently, Colamati et al. [6] studied ethanol electrooxidation on carbon supported Pt, Pt–Ru and $Pt_3Sn$ electrocatalysts in the temperature range 70–120 °C. They pointed out that Pt–Ru and $Pt_3Sn$ show about the same performance in a DEFC at 70 °C.

The aim of the present study is to systematically investigate the influence of different parameters, e.g., catalyst loading, ethanol concentration, electrode temperature, air or oxygen feed at the cathode, and different types of Pt-based anodes and cathodes (electrocatalysts), on DEFC

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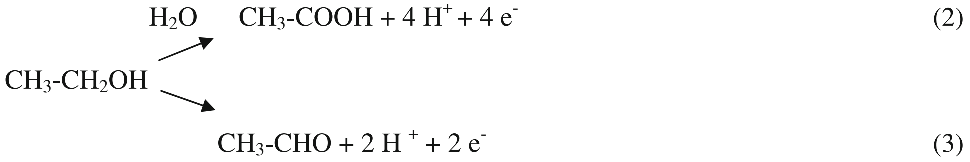
performance. Special emphasis is given to determining operating conditions such that the maximum power density is obtained with low catalyst loading. Cyclic voltammetry on individual electrodes is also conducted under the same conditions as for DEFC operation to analyse the power output. In previous studies, the influence of operating conditions on DEFC performance in conjunction with cyclic voltammetry has not been investigated.

The maximum energy from electrooxidation of ethanol is obtained if the oxidation reaction goes to completion. The complete oxidation of an ethanol molecule involves release of 12 electrons, as given by

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \quad (1)$$

At a higher operating temperature (>100 °C) a DEFC gives better performance with an enhancement of $CO_2$ formation. Below 100 °C, product analysis by chromatographic techniques (HPLC, GC) or by differential electrochemical mass spectrometry (DEMS) provided a detailed reaction mechanism of ethanol oxidation on Pt electrodes in acidic medium [7]. This involves parallel and consecutive oxidation reactions as follows:



$$CH_3\text{-}CH_2OH \xrightarrow{H_2O} CH_3\text{-}COOH + 4\,H^+ + 4\,e^- \quad (2)$$

$$CH_3\text{-}CH_2OH \rightarrow CH_3\text{-}CHO + 2\,H^+ + 2\,e^- \quad (3)$$

Reaction (2) occurs at higher electrode potentials [E > 0.8 V vs. RHE], where the water molecule is activated to form oxygenated species at the platinum surface. Reaction (3) occurs mainly at lower potentials (E < 0.6 V vs. RHE) [7].

## 2 Experimental

### 2.1 Materials

The catalysts used to prepare the anode and cathode were Pt/Ru (40%:20% by wt.)/C, Pt/C (40% by wt), and Pt-black high surface area (HSA, Johnson Matthey Inc., UK). Carbon paper (Lydall 484C-1, USA) was used as substrate for the catalyst powder. A Nafion® (SE-5112, DuPont USA) dispersion was used to cast the proton exchange membrane. A mixture of Nafion® and PTFE dispersion (DuPont India Pvt. Ltd.) was used as binder. Ethanol (Merck) was used as fuel. Pure cylinder oxygen (99.99% vol) and, in some cases, air was used as oxidant. Hydrogen peroxide and $H_2SO_4$ (Merck) was used for cleaning and protonation of the cast membrane. Isopropanol (Merck) was used as diluent.

### 2.2 Membrane preparation

The perfluorosulfonic acid membrane was cast from Nafion® dispersion (SE-5112, DuPont USA) containing 5-wt % Nafion ionomer. The isopropanol and Nafion dispersion was mixed in a 1:3 volume ratio and then set in an oven for 12 h in vacuum until all solvent evaporated and the polymeric ionomers formed a solid polymer membrane. The membrane film was treated for 1 h in boiling 3 vol. % $H_2O_2$ solution and for 1 h in 1 M $H_2SO_4$. Finally it was rinsed in boiling de-ionized water for 1 h. These treatments were carried out to remove the organic and metallic impurities and to protonate the cast membrane. The thickness of the resultant membrane was 145 μm.

### 2.3 Preparation of anode, cathode and membrane electrode assembly

Electrodes for DEFC should be porous in nature to ensure liquid fuel (ethanol) and gas (oxygen from air) diffusion through the anode and cathode active zones, respectively. The anode was prepared by dispersing the required quantity of Pt–Ru (40%:20% by wt.)/C or Pt-black HSA or Pt (40% by wt.)/C catalysts, activated carbon, and a mixture of Nafion ionomer and PTFE dispersion, which acted as binders. PTFE, along with pores at the anode, provides a flow network which allows easy escape of the reaction products from the anode. Further, the presence of PTFE in the anode decreases the crossover of ethanol from the anode side to the cathode side, resulting in higher cell performance. The anode slurry was first prepared by dispersing the required quantity of electrocatalyst powder in Nafion solution with a few drops of PTFE dispersion for 30 min using an ultrasonic water bath. The slurry was uniformly spread on a carbon paper in the form of a continuous wet film using a brush. It was then dried in an oven for 1 h at 80 °C. The cathode was prepared using similar compositions and methods as for the anode. The dried anode and cathode were sintered at 300 °C for 3 h to obtain the final form of the electrodes. The sintered electrodes were placed on either side of the cast Nafion membrane and hot pressed at a pressure of 10 kg cm$^{-2}$ for 2 min at 90 °C to prepare the membrane electrode assembly (MEA). The area of the MEA was 5 cm$^2$. Scanning electron micrographs (SEM) of the Pt–Ru/C anode and Pt-black HSA cathode are shown in Fig. 1.

## 2.4 Experimental setup and method

### *2.4.1 Half cell analysis*

Half cell analyses of the electrodes were preformed in a three-electrode cell assembly to obtain cyclic voltammograms. The working electrode was prepared from a long strip of carbon paper whose tip was coated with catalyst. The rest of the strip connected to the outside circuit. The cathode was immersed in the air-saturated electrolyte (0.5 M $HClO_4$), whereas, the anode was immersed in the ethanol and electrolyte (0.5 M $HClO_4$) solution saturated with nitrogen gas. Nitrogen was used to maintain an inert atmosphere. Nitrogen or air was supplied from the gas cylinder and purged through the solution using silicon tubing. The terminals of the electrodes were connected to a Potentiostat-Galvanostat (PGSTAT30, Autolab) for cyclic voltammetry. The potentiostat was connected to a computer which recorded all current–voltage data and General Purpose Electrochemical System (GPES) software was used to generate the voltammograms.

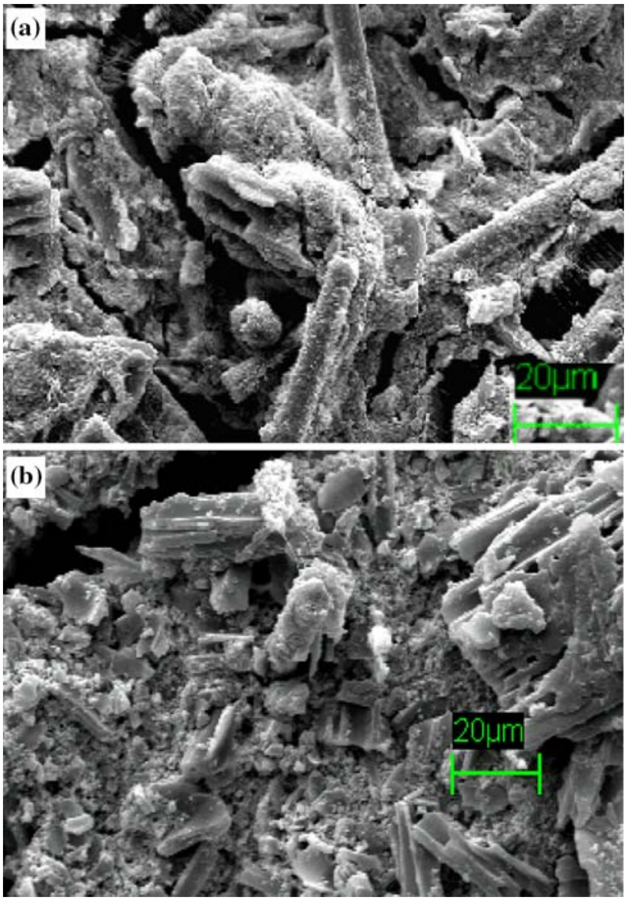


**Fig. 1** SEM of (**a**) 1 mg cm$^{-2}$ Pt–Ru/C anode, (**b**) 1 mg cm$^{-2}$ Pt-black HSA cathode

### *2.4.2 Direct ethanol fuel cell*

DEFC tests were performed with a single cell design (Fig. 2). The cell was fitted with a 5 cm$^2$ MEA clamped between two stainless steel blocks with serpentine flow channels of dimensions 2 × 2 mm for ethanol and oxygen/air flow. The cell was clamped between two mild steel plates using a set of retaining bolts positioned around the periphery of the cell. PTFE sheet and tape were used on both sides of the MEA for isolation and leakage prevention. Electrical heaters with control systems were placed behind each stainless steel block to heat the cell to the desired operating temperature. The pressure at the anode and cathode was maintained at 1 bar. Ethanol at different concentrations was fed to the anode at the rate of 1.2 mL min$^{-1}$ using a peristaltic pump. Oxygen or air was supplied from an oxygen cylinder or by an air blower to the cathode side. The data presented in the results and discussion section are for oxygen. Wherever air is used this is specifically mentioned. The current and voltage were recorded using multimeters (Sanwa) for different ethanol concentrations, electrode temperatures and different types of catalyst and loadings.

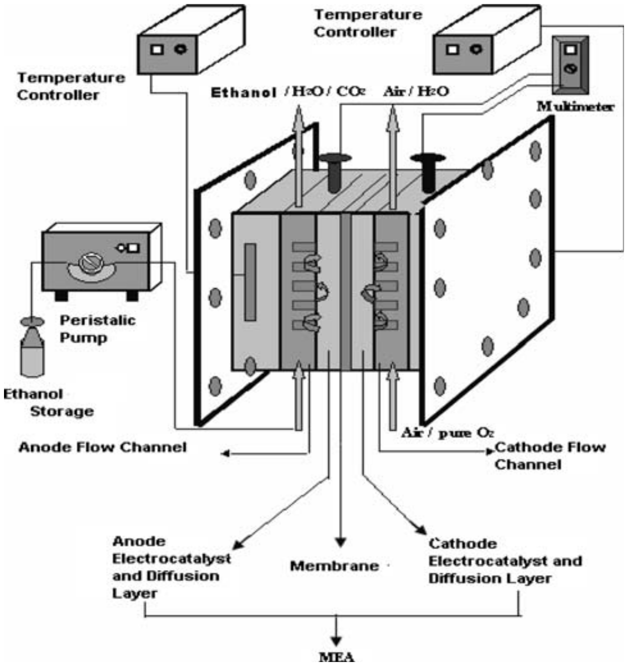


**Fig. 2** Schematic of direct ethanol fuel cell

## 3 Results and discussion

### 3.1 Effect of catalyst loading

Figure 3 shows the polarization curves and power density curves for different anode loadings from 0.6–1.5 mg $cm^{-2}$ Pt–Ru/C, for a fixed cathode loading of 1 mg $cm^{-2}$ Pt-black HSA. 2 M ethanol was used as the fuel and the temperature was 42 °C at the anode and cathode. It is seen that the voltage and power density are at a maximum for a given current density when an anode loading of 1 mg $cm^{-2}$ is used. A maximum power density of 7.83 mW $cm^{-2}$ was obtained for 1 mg $cm^{-2}$ Pt–Ru/C loading at the anode. However, cell performance decreased with increase in anode loading to 1.5 mg $cm^{-2}$. The reason for this decrease may be catalyst agglomeration at higher loading in a given specific volume of the electrode. Agglomeration results in a decrease in porosity of the catalyst layer leading to increased diffusional resistance to mass transport of fuel. These observations have been explained by Pramanik and Basu [8].

The above mentioned dependence of cell performance on catalyst loading is similar to that obtained from cyclic voltammetry (CV). Figure 4 shows the CV at a scan rate of 25 mV $s^{-1}$ with the same range of Pt–Ru/C loadings. The conditions in the CV experiment were the same as that of the DEFC experiment. It is seen that 1 mg $cm^{-2}$ of Pt–Ru/C gives a slightly higher oxidation peak compared to that obtained for 0.5 mg $cm^{-2}$ and 1.5 mg $cm^{-2}$ Pt–Ru/C loadings. A Pt–Ru/C loading of 1 mg $cm^{-2}$ results in 132 mA $cm^{-2}$ current density, at 0.095 V, whereas 0.5 mg $cm^{-2}$ and 1.5 mg $cm^{-2}$ give oxidation peaks at 0.075 V and 0.031 V at current densities of 109.6 mA $cm^{-2}$ and 114.6 mA $cm^{-2}$, respectively.

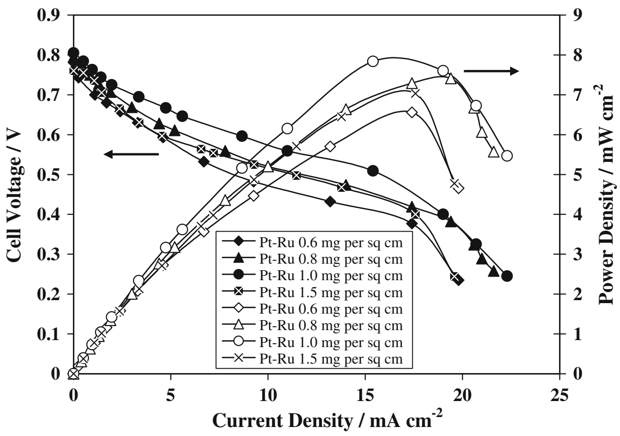


**Fig. 3** Comparison of current density versus cell voltage and current density versus power density for 2 M ethanol and at different anode (Pt–Ru/C) loadings with cathode (Pt-black HSA) loading of 1.0 mg $cm^{-2}$ and at a 42 °C cell temperature

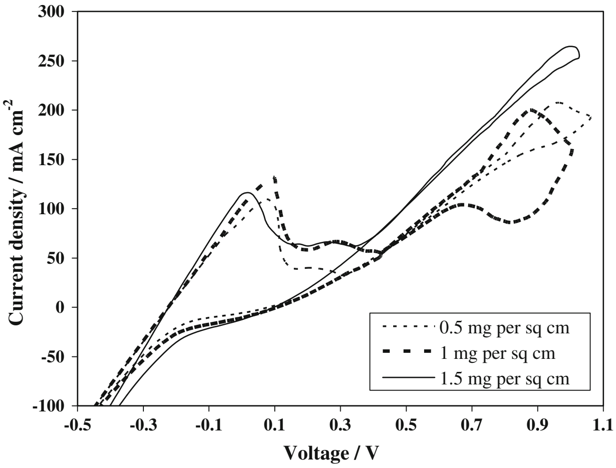


**Fig. 4** CV for different Pt–Ru/C anode loadings at 25 mV $s^{-1}$ scan rate using 2 M ethanol in 0.5 M $HClO_4$, at 42 °C

A similar trend was observed when the cathode (Pt-black HSA) loading was varied and the anode (Pt–Ru/C) loading was fixed at 1 mg $cm^{-2}$. The DEFC performance on cathode loading variation is shown in Fig. 5. The maximum power density of 10.30 mW $cm^{-1}$ at a current density of 23.5 mA $cm^{-2}$ and OCV of 0.815 V was obtained with 2 M ethanol, a 90 °C anode and 60 °C cathode temperature and with the loading of the anode (Pt–Ru/C) and cathode (Pt-black HSA) at 1 mg $cm^{-2}$. However, cell performance decreased upon increasing the cathode (Pt-black HSA) loading to 1.5 mg $cm^{-2}$. Although not shown here, the CV for cathode loading variation substantiates the aforementioned DEFC experiment.

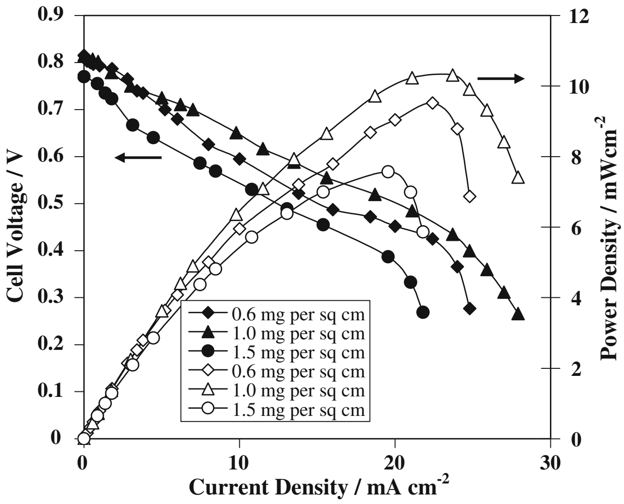


**Fig. 5** Comparison of current density versus cell voltage and current density versus power density for 2 M ethanol and at different cathode (Pt-black HAS) loadings with anode (Pt–Ru/C) loading of 1.0 mg $cm^{-2}$ and at a 90 °C anode and 60 °C cathode

### 3.2 Effect of ethanol concentration

Figure 6 shows the polarization and power density curves for optimum anode (Pt–Ru/C) and cathode (Pt-black HSA) loading of 1 mg cm$^{-2}$ at different ethanol concentrations. The temperature at the anode and cathode was maintained at 42 °C. The voltage and power density for a given current density increase with increase in ethanol concentration. However, cell performance decreases when the ethanol concentration is increased from 2 to 3 M. Figure 6 shows that 2 M ethanol results in a maximum power density of 7.85 mW cm$^{-2}$ at a current density of 18 mA cm$^{-2}$, whereas 3 M ethanol generates 6.58 mW cm$^{-2}$ at 15 mA cm$^{-2}$. Similar observations were made when the anode catalyst was changed from Pt–Ru/C to Pt-black HSA (Fig. 7). A maximum power density of 6.85 mW cm$^{-2}$ was obtained for a Pt-black HSA loading of 1 mg cm$^{-2}$ at the anode with the use of 2 M ethanol at 42 °C. Although not shown here, the power density reached a maximum when 2 M ethanol with 1 mg cm$^{-2}$ of Pt/C was used at the anode. Initially, increase in ethanol concentration increases the current density and OCV because the overpotential is reduced. However, at a higher ethanol concentration, the coverage of the electrode catalyst by ethanol increases and, at the same time, the water concentration in the solution decreases. It is shown in the reaction mechanism (Eq. 2) that the presence of a water molecule is essential in the electrooxidation of ethanol. Further, a higher ethanol concentration in the anode feed leads to a higher concentration gradient across the interface of the anode and polymer electrolyte membrane, leading to increased crossover through the Nafion® membrane. Thus, a delicate balance is required between ethanol oxidation kinetics and ethanol crossover to enhance the performance of a DEFC in the activation and ohmic-controlled regions [9].

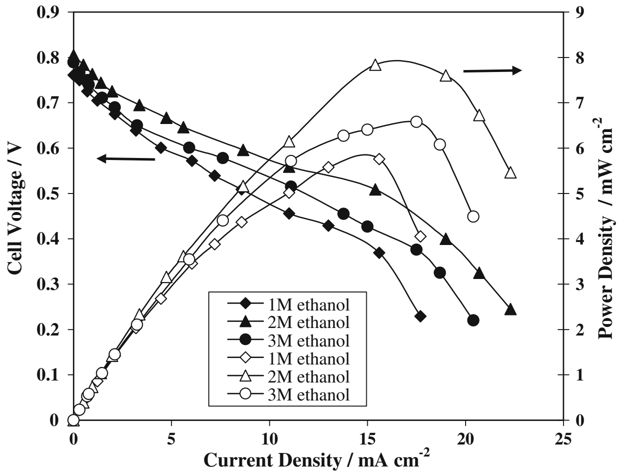


**Fig. 6** Comparison of current density versus cell voltage and current density versus power density at different ethanol concentrations with 1.0 mg cm$^{-2}$ Pt–Ru/C anode and 1.0 mg cm$^{-2}$ Pt-black HSA cathode, at 42 °C

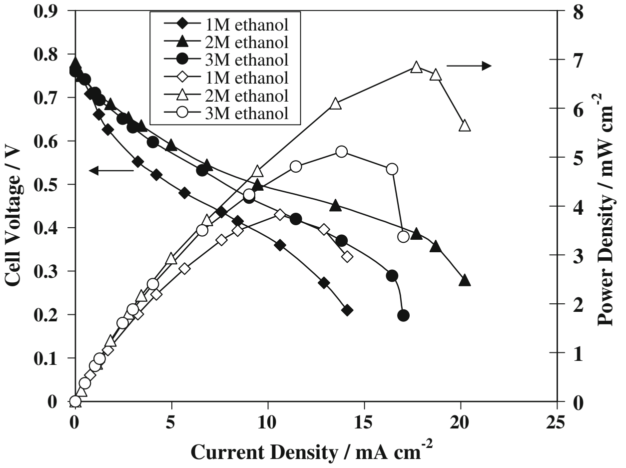


**Fig. 7** Comparison of current density versus cell voltage and current density versus power density at different ethanol concentrations with 1 mg cm$^{-2}$ Pt-black HSA on both anode and cathode, at 42 °C

Figures 8 and 9 show CVs for the Pt–Ru/C and Pt-black HSA anodes in the presence of varying ethanol concentrations. The CV tests were conducted under the same conditions as that for the DEFC. 2 M ethanol gives a higher oxidation peak than 1 M and 3 M ethanol for both Pt–Ru/C and Pt-black HSA. A similar trend was also observed for the CV for Pt/C (not shown here).

### 3.3 Effect of different types of anode and cathode catalysts

Figure 10 shows the current density and power density curves for different anode catalysts (1 mg cm$^{-2}$ loading) with air or oxygen at the cathode. In general, the Pt–Ru/C anode generates a higher voltage and power density at a given current density compared to that produced by

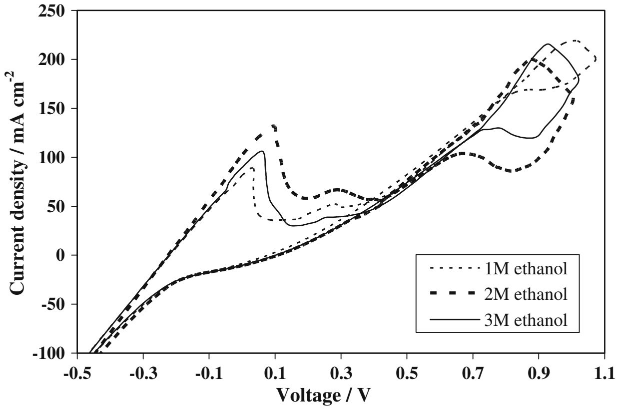


**Fig. 8** CV for different ethanol concentrations in 0.5 M $HClO_4$ at 25 mV s$^{-1}$ scan rate for 1 mg cm$^{-2}$ Pt–Ru/C anode, at 42 °C

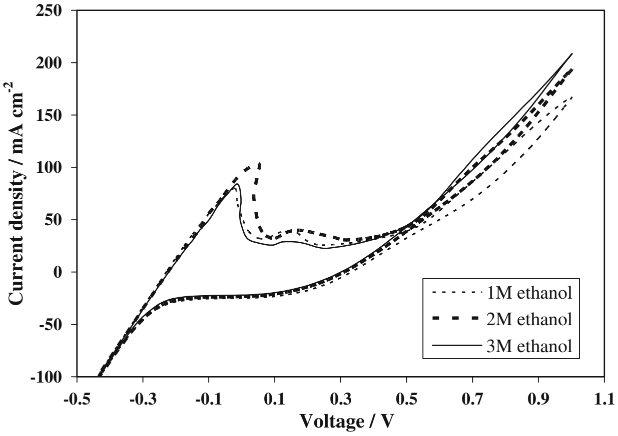


**Fig. 9** CV for different ethanol concentrations in 0.5 M $HClO_4$ at 25 mV $s^{-1}$ scan rate for 1 mg $cm^{-2}$ Pt-black HSA anode, at 42 °C

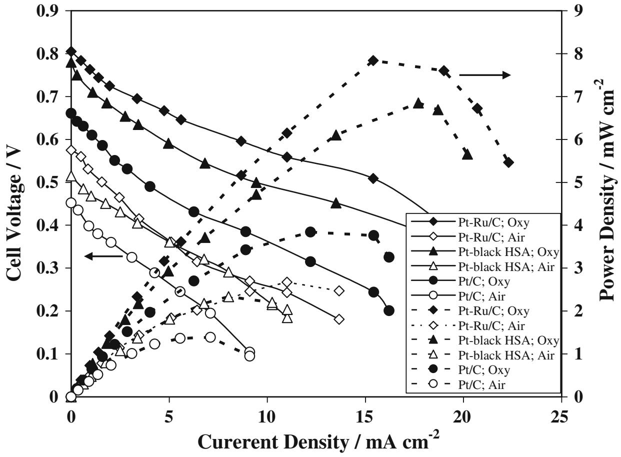


**Fig. 10** Comparison of current density versus cell voltage and current density versus power density for 2 M ethanol using Pt–Ru/C, Pt-black HSA, Pt/C as anode (1 mg $cm^{-2}$ loading) and Pt-black HSA as cathode (1 mg $cm^{-2}$ loading) at 42 °C. Oxy = oxygen at cathode and Air = air at cathode

Pt-black HSA or Pt/C anodes. The cathode catalyst used was Pt-black HSA. The temperatures of the anode and cathode sides were maintained at 42 °C. This performance was observed irrespective of the use of oxygen or air as the oxidant at the cathode. Pt–Ru/C showed a higher activation towards ethanol electrooxidation as compared to Pt-black HSA and Pt/C because of the bi-functional mechanism of ethanol oxidation in the presence of Pt–Ru/C [5]. The cleavage of the C–C bond in the ethanol molecule takes place on the platinum active sites by a chemisorption mechanism. At the same time, dissociation of water molecules takes place at lower potential on the ruthenium surface giving $OH_{ads}$ species that oxidize the residues of chemisorbed ethanol completely to $CO_2$ [5].

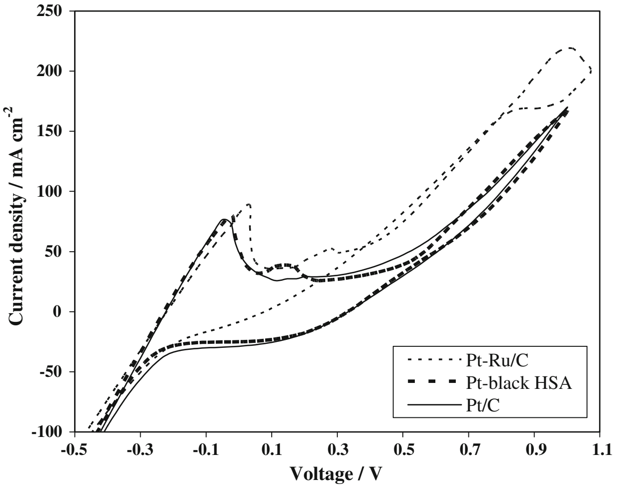


**Fig. 11** CV for Pt–Ru/C, Pt-black HSA and Pt/C anode in the presence of 1 M ethanol in 0.5 M $HClO_4$ solution with scan rate of 25 mV $s^{-1}$, at 42 °C

Figure 11 shows the CV for Pt–Ru/C, Pt-black HSA and Pt /C electrocatalysts (1 mg $cm^{-2}$) in the presence of 1 M ethanol in 0.5 M $HClO_4$ at 42 °C. The Pt–Ru/C anode gives a slightly higher oxidation peak than that for Pt-black HSA and Pt/C. The Pt–Ru/C anode gives an oxidation peak at 0.034 V at 89 mA $cm^{-2}$, whereas those for Pt-black HSA and Pt/C are −0.002 V and −0.049 V at current densities of 80 mA $cm^{-2}$ and 76 mA $cm^{-2}$, respectively. The CV shows that the Pt–Ru (40%:20% by wt.)/C electrode-catalyst is more active compared to the other catalysts tested. It should be noted that the activation overpotential is slightly higher for Pt–Ru (40%:20% by wt.)/C catalysts than for Pt-black HSA and Pt/C at 76 mA $cm^{-2}$.

Figure 12 shows the current density versus voltage and power density plot for different cathode catalysts tested against a fixed anode catalyst (1 mg $cm^{-2}$ of Pt–Ru/C) in

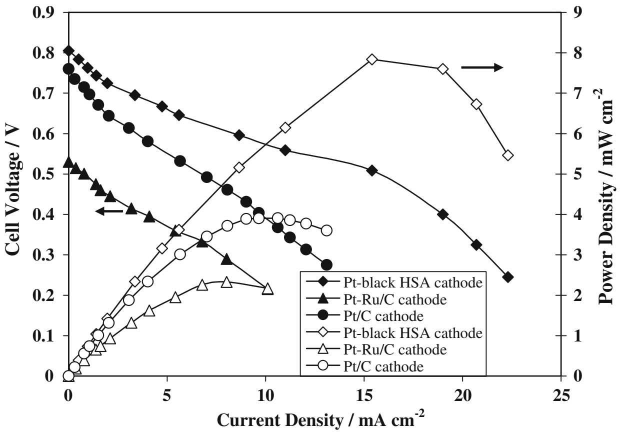


**Fig. 12** Comparison of current density versus cell voltage and current density versus power density for 2 M ethanol using Pt–Ru/C, Pt-black HSA, Pt/C as cathode (1 mg $cm^{-2}$ loading) and Pt–Ru/C as anode (1 mg $cm^{-2}$ loading), at 42 °C

DEFC. The temperature was maintained at 42 °C and oxygen was used as the cathode feed. The use of Pt-black HSA as a cathode results in a higher power density for a given current density compared to that obtained with Pt–Ru/C and Pt/C as the cathode. Pt-black HSA provides a higher active surface area (72 $m^2$ $gm^{-1}$) compared to other cathode catalysts (27 $m^2$ $gm^{-1}$) tested. Although the CV of the oxygen reduction reaction (ORR) using different cathode electrocatalysts is not discussed here, the Pt-black HSA cathode showed a higher ORR peak compared to Pt–Ru/C and Pt/C. Details of the ORR are discussed elsewhere [10–12].

### 3.4 Effect of different anode and cathode temperatures

Figure 13 compares the polarization and power density curves for different temperature ranges of the anode (42–120 °C) and cathode (42–88 °C). (The temperature combinations used at the anode and cathode are given in the legend of Fig. 13). It should be noted that the cell was operated under a temperature gradient. Pt–Ru/C and Pt-black HSA were the anode and cathode, respectively, and were used with 2 M ethanol solution as the feed to the anode and oxygen to the cathode. Initially, the power density increases with increase in anode (90 °C) and cathode (60 °C) temperature and then decreases with further increase in temperature (anode, 120 °C and cathode, 88 °C). It is well known that the anode and cathode kinetics improve with increase in temperature and, hence, overpotential decreases and power density increases. However, the polymer electrolyte membrane becomes dry as the anode temperature increases, leading to a decrease in proton conductivity. Therefore, the maximum power density drops from 10.30 mW $cm^{-2}$ at a 90 °C anode to 7.9 mW $cm^{-2}$ at a 120 °C anode. A similar dependence of power density on temperature was obtained for different combinations of anode and cathode catalysts. The effect of temperature on cell performance is well understood for PEM based fuel cells (PEMFC). It should be noted that the behaviour of a liquid fed DEFC is different from that of a PEMFC. Feeding an ethanol–water solution to a DEFC enhances membrane hydration. Operation of a DEFC above 100 °C with composite membranes capable of water retention has been demonstrated [13].

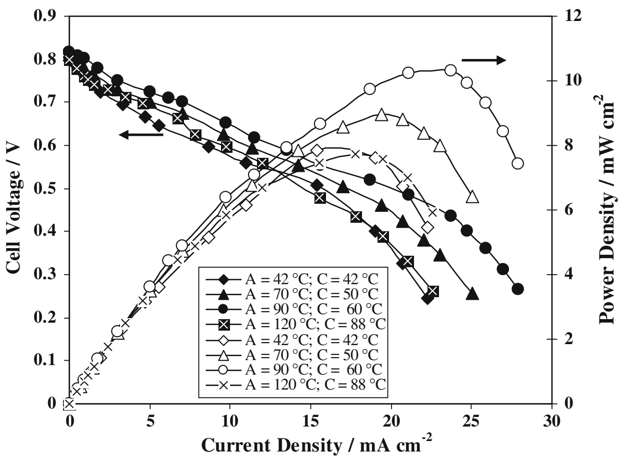


**Fig. 13** Comparison of current density versus cell voltage and current density versus power density at different anode and cathode temperatures using 2 M ethanol. Anode (A) loading: 1.0 mg $cm^{-2}$ Pt–Ru/C; Cathode (C) loading: 1.0 mg $cm^{-2}$ Pt-black HSA

## 4 Conclusions

A DEFC was systematically studied to determine the optimum conditions of cell operation such that maximum performance was obtained. CVs were conducted to substantiate the results obtained on DEFC experiments. The maximum OCV at a temperature of 90 °C at the anode and 60 °C at the cathode, 2 M ethanol, and a pure oxygen supply at the cathode was 0.815 V. Pt–Ru/C shows the highest activity towards ethanol oxidation compared to Pt-black HSA and Pt/C. Pt-black HSA is the best cathode catalyst among the Pt-based catalysts tested. The maximum power density, 10.3 mW $cm^{-2}$, was obtained with 2 M ethanol, oxygen feed at the cathode, a 1 mg $cm^{-2}$ Pt–Ru/C anode at 90 °C and a 1 mg $cm^{-2}$ Pt-black HSA cathode at 60 °C. Initially, the cell performance increases with increase in catalyst loading and then decreases slightly with further increase in loading. Increase in ethanol concentration increases the current density and OCV. However, higher ethanol concentration (3 M) reduces cell performance. DEFC performance increases with increase in anode temperature to 90 °C and cathode temperature to 60 °C then decreases as the anode temperature is increased to 120 °C and cathode temperature to 88 °C, with Nafion® (SE5112) as solid polymer electrolyte. The results obtained from DEFC experiments correspond to those obtained from CVs of individual electrodes under the same conditions.

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