

Short communication

Direct alkaline fuel cell for multiple liquid fuels: Anode electrode studies

A. Verma^a, S. Basu^{b,*}

^a Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India

^b Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz-Khas, New Delhi 110016, India

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Abstract

A direct alkaline fuel cell with a liquid potassium hydroxide solution as an electrolyte is developed for the direct use of methanol, ethanol or sodium borohydride as fuel. Three different catalysts, e.g., Pt-black or Pt/Ru (40 wt.%:20 wt.%) /C or Pt/C (40 wt.%), with varying loads at the anode against a MnO₂ cathode are studied. The electrodes are prepared by spreading the catalyst slurry on a carbon paper substrate. Nickel mesh is used as a current-collector. The Pt–Ru/C produces the best cell performance for methanol, ethanol and sodium borohydride fuels. The performance improves with increase in anode catalyst loading, but beyond 1 mg cm⁻² does not change appreciably except in case of ethanol for which there is a slight improvement when using Pt–Ru/C at 1.5 mA cm⁻². The power density achieved with the Pt–Ru catalyst at 1 mg cm⁻² is 15.8 mW cm⁻² at 26.5 mA cm⁻² for methanol and 16 mW cm⁻² at 26 mA cm⁻² for ethanol. The power density achieved for NaBH₄ is 20 mW cm⁻² at 30 mA cm⁻² using Pt-black.

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1. Introduction

Alkaline fuel cells (AFCs) are amongst the most matured of fuel cell technologies. The systems were used in the 1960s and 1970s by NASA in the Apollo and Space Shuttle programs [1]. The fuel cells on these spacecrafts provided electrical power for onboard systems, as well as drinking water. Since then, AFCs have lost their popularity to other new emerging fuel cell technologies such as the proton-exchange membrane fuel cell (PEMFC) for vehicular applications because of the flexibility of using a solid electrolyte and the avoidance of electrolyte leakage. The PEMFC does, however, have various drawbacks. In fact, it is understood that all the fuel cells have some advantages and some disadvantages. Interest in the alkaline fuel cell has arisen again because of its better oxygen reduction kinetics in alkaline condition than in acidic environment, simplicity, low cost, and comparable efficiency compared with other types of fuel cell [2]. The use of an alkaline electrolyte provides many benefits such

as higher efficiency [3] and a wider selection of possible electrode catalysts and fuels. The electrocatalysts used in the alkaline fuel cell are platinum [4,5], nickel [3,6], Fe(III) [7], Al(III) [7], Pt/Ru [8], while fuels are hydrogen [4], methanol [5,9], ethanol [9] and sodium borohydride [10,11]. Koscher and Kordesch [5] reported the experimental work of Vieltich, in which 10 M KOH and 4.5 M methanol were employed as an electrolyte and fuel, respectively. Platinum (2–5 mg cm⁻²) and electrocatalytically active carbon were used as the anode and the cathode catalyst, respectively. The open-circuit voltage was 0.9 V and the current density was 2 mA cm⁻² at 0.6–0.75 V. They also reported the use of a third electrode as a grid to minimize the methanol crossover to the cathode side. The anode consisted of an un-sintered Ag/PbO catalyst for methanol oxidation, the cathode was a platinumized carbon/PTFE bonded structure, and platinum-catalyzed nickel served as a grid electrode. A mixture of 6 M methanol and 9 M KOH solution was used as an anolyte and 9 M KOH solution as catholyte, which were separated by an anion-exchange membrane. The best performance achieved with a single cell ranged from 0.6 to 0.7 V at 6 mA cm⁻². Prabhuram and Manoharan [12] investigated methanol oxidation on platinum electrodes in KOH solution using half-cell analysis. They recorded cyclic

* Corresponding author. Tel.: +91 11 26591035; fax: +91 11 26581120.

E-mail address: sbasu@chemical.iitd.ernet.in (S. Basu).

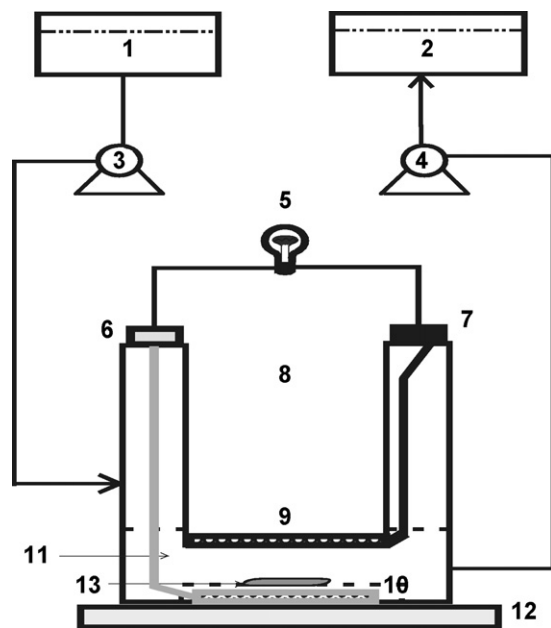


Fig. 1. Schematic diagram of a direct alkaline fuel: (1) fuel–electrolyte mixture storage; (2) exhausted-fuel–electrolyte mixture storage; (3 and 4) peristaltic pumps; (5) load; (6) anode terminal; (7) cathode terminal; (8) air; (9) cathode electrode; (10) anode electrode; (11) fuel and electrolyte mixture; (12) magnetic stirrer; (13) anode shield.

voltammograms in different electrolyte concentrations in the presence or absence of different methanol concentrations. The methanol oxidation reaction was carried out in different electrolyte/methanol mixtures and it was highest for a 6 M KOH/6 M CH₃OH mixture. Detailed studies on direct alcohol alkaline fuel cells have been elaborately discussed by Basu [13] and Verma et al. [14].

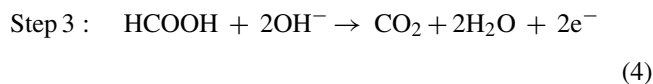
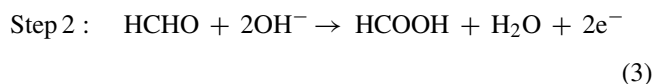
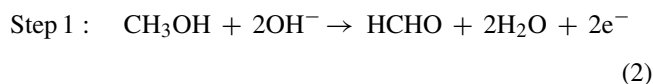
Although different electrode catalysts and fuels are used in direct alcohol alkaline fuel cells, there have been no systematic studies conducted on the effect of the type and loading of various noble metal catalyst at the anode as well as the direct use of different fuels on the performance. In the present investigation, a direct alkaline fuel cell is developed and experiments are performed to study the effect of catalyst type and loading at the anode. A MnO₂ cathode is used together with three different fuels, e.g., methanol, ethanol and sodium borohydride. The fuel cell is operated with a mixture of 2 M fuel/3 M electrolyte concentration as this was found to be the optimum concentration in a similar experimental set-up and operating conditions [15].

The detailed reaction mechanisms for the three fuels in the presence of an alkaline electrolyte and a Pt/Ni anode [16] are described below. The reaction at the cathode is same irrespective of the fuel employed. The reaction at the cathode is given by:



The reaction at the anode for different fuels is expressed by the following.

- Methanol



The major problem with methanol, when using an alkaline electrolyte, is that the carbon dioxide produced reacts with the electrolyte to form potassium carbonate, i.e., $CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$. This gradually consumes the electrolyte. Further, it has been documented [17] that if the cathode feed is contaminated by carbon dioxide, carbonate may form at the cathode and the performance of the AFC may decrease. Gülzow and Schulze [18] investigated the long-term behaviour of alkaline fuel cell (AFC) electrodes supplied with CO₂-containing gases. No evidence was obtained to suggest that CO₂ affects significantly the degradation process. Recently, Gülzow et al. [1] reviewed the effect of carbon dioxide on the performance of an AFC and found that there was slight degradation in performance but there was no adverse effect due to the presence of CO₂ either in the air or produced by methanol as a fuel in the AFC. Nevertheless, the electrolyte can be recycled to remove the carbonate formed and also periodically recharged with fresh KOH.

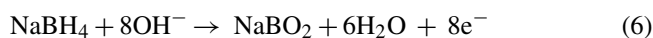
- Ethanol



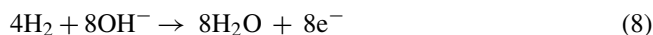
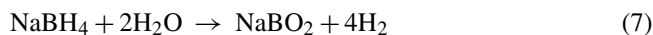
In the case of ethanol, the reaction is not allowed to proceed further and thus CO₂ is not generated. Thus, the problem of carbonate formation does not arise. The electrons generated are less than those in the electro-oxidation of methanol.

- Sodium borohydride

There are two possible routes for the oxidation of NaBH₄. In the first route, NaBH₄ is directly oxidized [10,11]:



In the second route, hydrogen is liberated at high temperature and a pH less than 7.



The hydrogen produced by this route may escape from the system thus the fuel may not be fully utilized.

2. Experimental

2.1. Materials

The catalysts used to prepare the anodes were Pt-black, Pt/C (40 wt.%) and Pt/Ru (40 wt.%, 20 wt.%) / C procured from

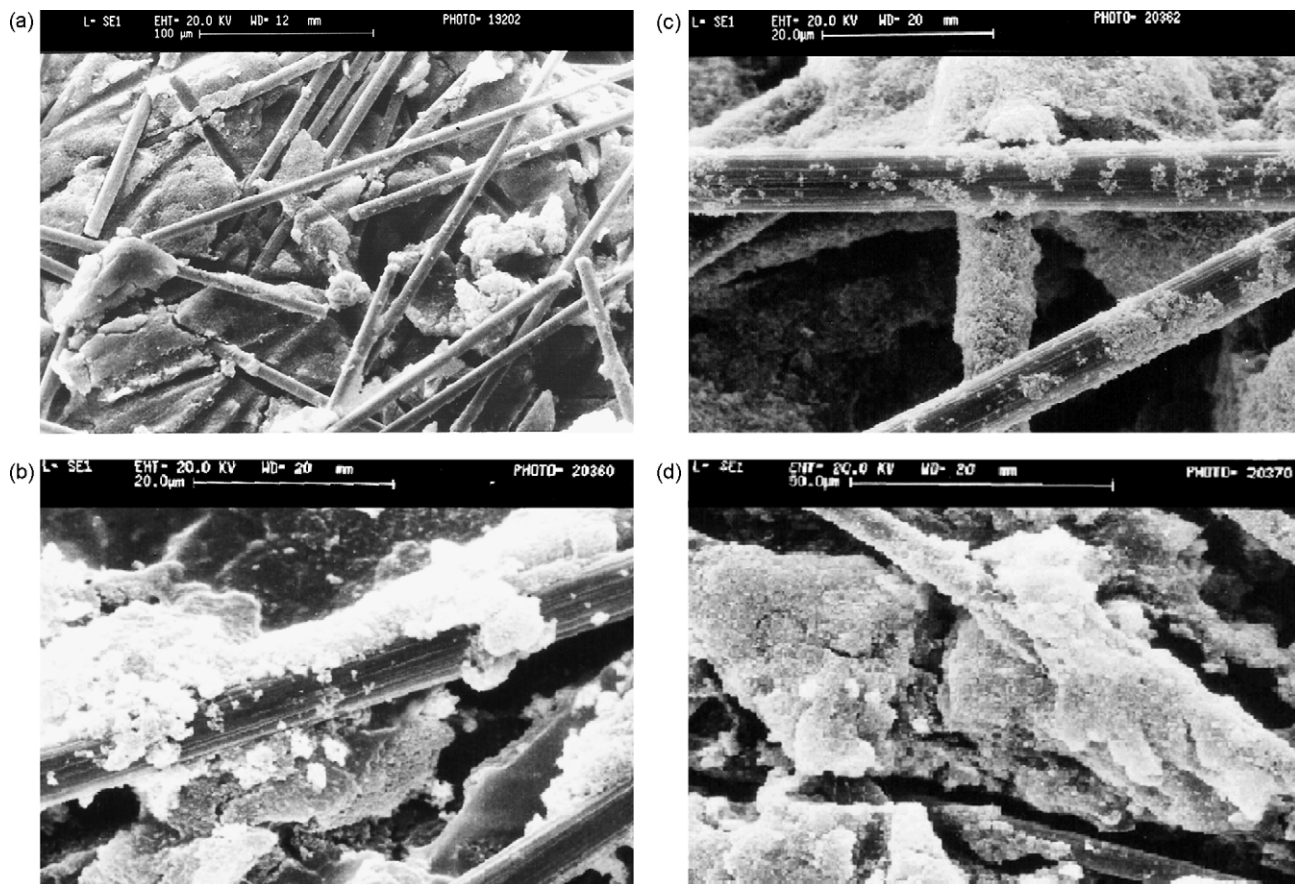


Fig. 2. (a) SEM of carbon paper (Lydall 484C-1) substrate; (b) SEM of Pt-black catalyzed electrode; (c) SEM of Pt/C (40 wt.%), catalyzed electrode; (d) SEM of Pt/Ru (40 wt.%:20 wt.%)C catalyzed electrode.

Johnson Matthey Inc., UK. The cathode was prepared from manganese dioxide (E. Merck). Carbon paper (484C-1 Lydall, USA) was used as a substrate for the catalyst particles. Nafion[®] (SE-5112) and Teflon[®] dispersions were obtained from DuPont, USA. Pure-nickel mesh was employed as a current-collector because it is highly resistive to alkali and is a good electrical conductor. The anolyte chamber was made from either plastic or glass, while the catholyte chamber was made from plastic. Analytical grade of methanol, ethanol and sodium borohydride were obtained from E. Merck. Potassium hydroxide for the electrolyte and was obtained from Qualigen Fine Chemicals, India. Freshly prepared distilled water was used in all experiments.

2.2. Electrode preparation

The anode electrode was prepared by first dispersing the required quantity of catalyst powder in a Nafion[®] dispersion (SE-5112) for 30 min. An ultrasonic water bath was used to prepare catalyst slurry. The Nafion[®] dispersions have both hydrophilic and hydrophobic features. PTFE is hydrophobic and when employed as a binder, it may prevent hydrophilic fuel from reaching the catalyst site. Therefore, Nafion[®] has been used to bind the catalyst particles on to the carbon paper. The catalyst slurry was spread on carbon paper in the form of a continuous wet film using a paint-brush technique. It was then dried in an oven for 30 min at 80 °C. Nickel mesh was used as a current-collector

because of its non-corrosive nature in an alkaline medium. The catalyzed carbon paper was pressed on to the nickel mesh with application of the Teflon[®] dispersion. The prepared electrode was pressed at 50 kg cm⁻² and 120 °C for 5 min to form a composite structure. The area of the working electrode was 10 cm². Finally, the composite was heated at 573 K for 4 h to obtain the final form of the anode electrode [15]. Scanning electron micrographs (SEMs) of the anode catalyst electrode provided information the morphological structure of the electrode. The cathode electrode was prepared with 3 mg cm⁻² of MnO₂ catalyst and the same procedure was followed as explained by Verma et al. [19] for a similar experimental set-up and conditions.

2.3. Experimental set-up

A schematic diagram of the experimental set-up is shown in Fig. 1. The diameter of the anodic chamber is 6 cm and length is 7 cm. The cathode chamber has slightly smaller dimensions, namely, 4 cm and 5.5 cm, respectively. A hollow cylinder containing cathode, attached to one side, was placed inside a beaker. The anode was placed at the bottom of the beaker. The space between the anode and the cathode was filled with the mixture of electrolyte and fuel. A combine volume of 60 ml for the fuel plus alkali medium was used in the experiments. The fuel cell was kept in a water bath (not shown in Fig. 1)

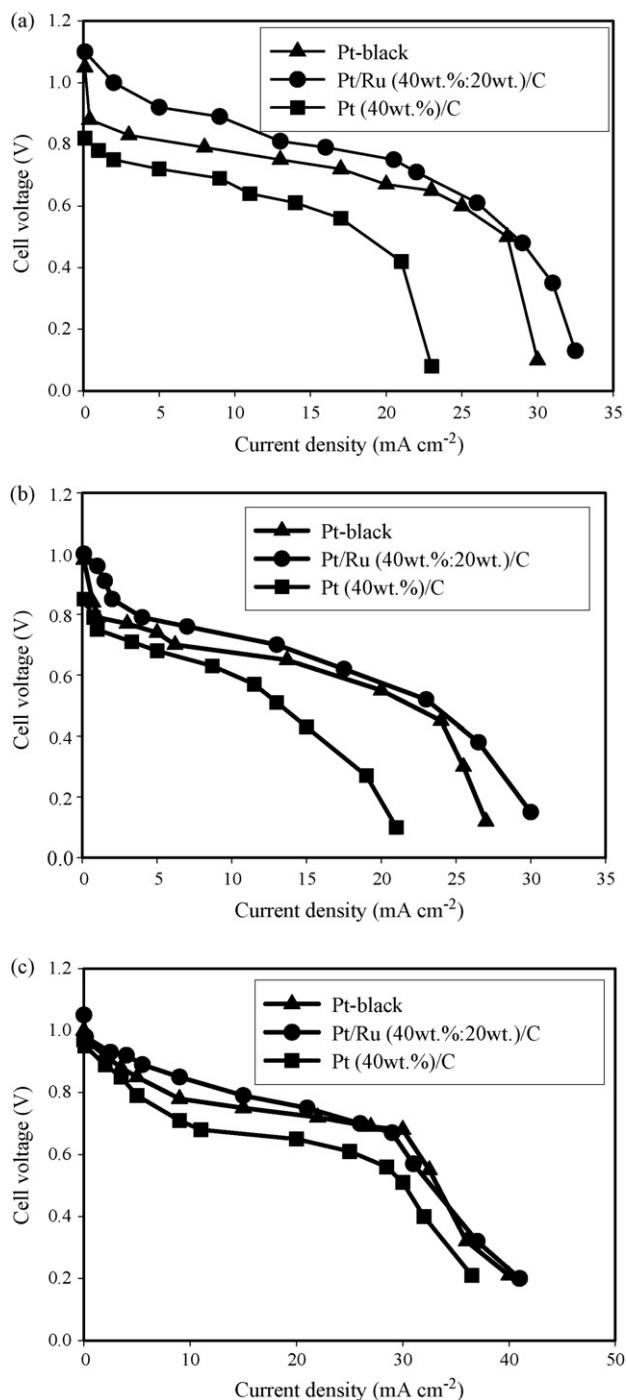


Fig. 3. Current density–cell voltage characteristics for (a) 2 M methanol/3 M KOH solution for different catalysts at 25 °C; (b) 2 M ethanol/3 M KOH solution for different catalysts at 25 °C; (c) 2 M sodium borohydride/3 M KOH solution for different catalysts at 25 °C; cathode: MnO_2 .

to maintain a constant temperature. The fuel–electrolyte mixture was stored in a tank and was connected to the inlet of the fuel cell by a flexible tube through a peristaltic pump. The outlet of the fuel cell was connected to the exhaust-fuel storage tank by a flexible tube through a peristaltic pump. A magnetic stirrer was used to maintain uniformity of the fuel–electrolyte mixture [9,15]. To protect the anode from the revolving magnet, the anode was shielded by means of a perforated plastic

support. Stirring of the fuel and electrolyte mixture dissolves uniformly any carbonate formed at the anode or the cathode. Apart from stirring, the continuous supply of feed and the removal of exhausted fuel and electrolyte mixture from the cell helps to reduce the carbonate ion concentration and it never reaches a precipitation level during the experimental work. The terminals of the cell were connected to a digital multimeter (Sanwa PC5000, Japan). The fuel and electrolyte solution were maintained up to a certain level such that one side of the cathode was in contact with electrolyte while the other side was exposed to air. Oxygen present in air acted as the oxidant.

2.4. Fuel cell operation

The fuel cell was fed with a mixture of a 2 M concentration of fuel (methanol or ethanol or sodium borohydride) and a 3 M electrolyte (KOH) concentration from the storage tank at a rate of 1 ml min^{-1} . The solution was stirred continuously with a magnetic stirrer, which was located on the perforated anode shield. The heat of the reaction is carried out of the fuel cell with the un-reacted fuel, products and electrolyte mixture. The open-circuit voltage (OCV) and short-circuit current were measured with a multimeter. The voltage and corresponding current were measured under variable load conditions to obtain a j – v (current density–cell voltage) characteristic curve. The steady-state values of voltage and current were recorded in all experiments. The effects of different catalyst (Pt/C, Pt-black and Pt/Ru/C) and the catalyst loading on fuel cell performance were studied for methanol, ethanol and sodium borohydride fuels. All the experiments were performed at 25 °C.

3. Results and discussion

3.1. Electrode morphology

A scanning electron micrograph of the carbon paper (Lydall 484C-1) substrate on which the anode catalyst is placed is given in Fig. 2a. This shows that the carbon paper is made of rod-like carbon fibre and carbon powder compressed together. Fig. 2b–d present SEMs of anode electrodes with different catalysts, e.g., Pt-black, Pt/C (40 wt.%) and Pt/Ru (40 wt.%,20 wt.)/C. All the SEMs are for a catalyst loading of 1 mg cm^{-2} . Fig. 2b reveals that Pt-black is more or less evenly distributed on the carbon paper substrate, except for a few places where agglomeration of the Pt-black catalyst has occurred. Fig. 2c shows that the Pt/C (40 wt.%) catalyst is uniform with very little agglomeration. The carbon fibres are covered by the fine particles of the catalyst powder. On comparing the Pt/C (40 wt.%) (Fig. 2c) and Pt-black electrodes (Fig. 2b), it is seen that the deposited Pt/C particles are finer than the Pt-black particles. As the Pt-black particles are smaller than the Pt/C particles, perhaps some Pt-black particles may have been deposited in an agglomerated form. Fig. 2d shows that the Pt/Ru (40 wt.%,20 wt.)/C catalyst is uniformly spread over the carbon paper substrate.

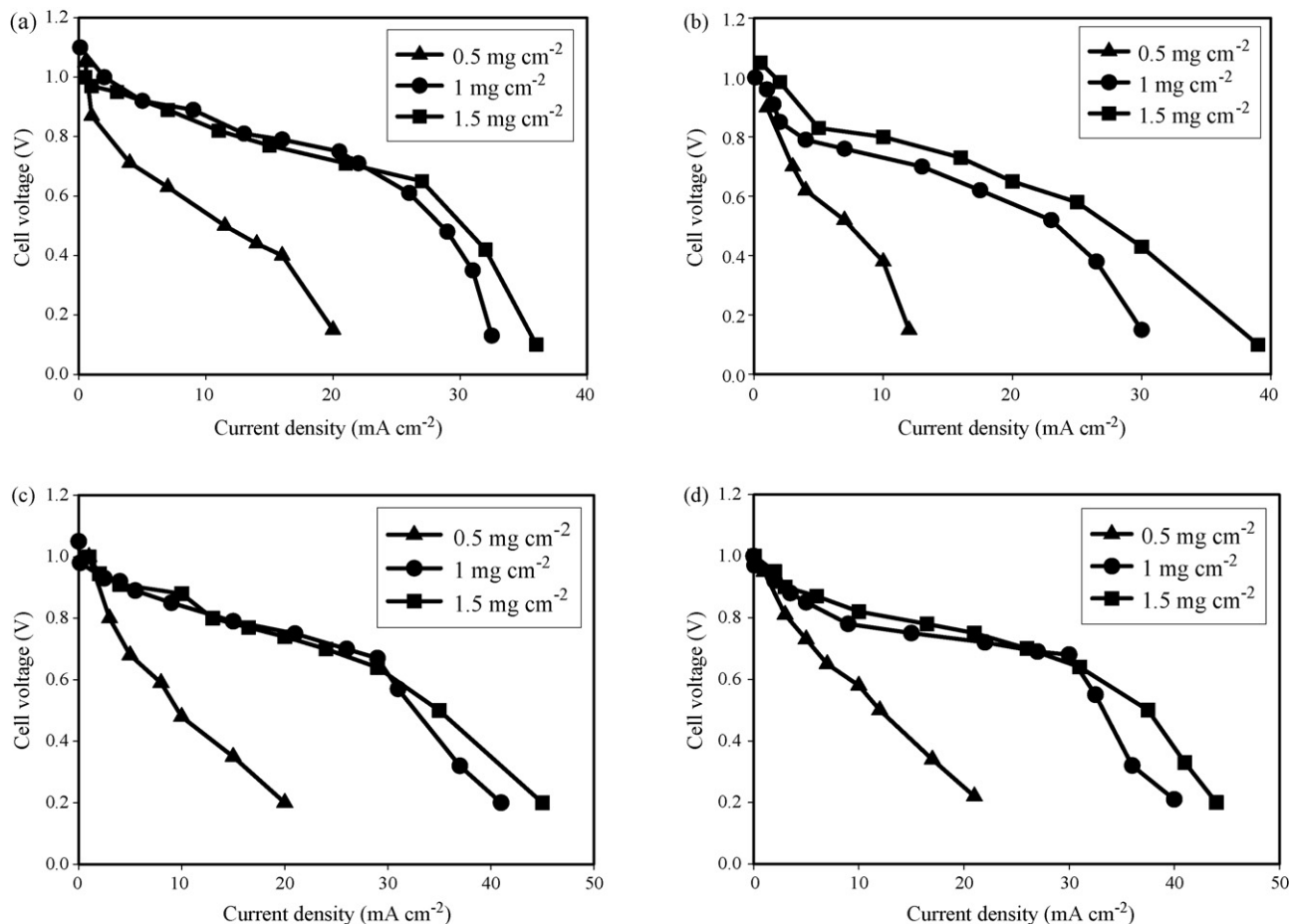


Fig. 4. Current density–cell voltage characteristics for (a) 2 M methanol/3 M KOH solution at different loading of Pt/Ru (40 wt.%,20 wt.%) /C at anode for direct alkaline fuel cell; (b) 2 M ethanol/3 M KOH solution at different loading of Pt/Ru (40 wt.%,20 wt.%) /C at anode for direct alkaline fuel cell; (c) 2 M sodium borohydride/3 M KOH solution at different loadings of Pt/Ru (40 wt.%,20 wt.%) /C at anode for direct alkaline fuel cell; (d) the variation of Pt-black anode catalyst for 2 M sodium borohydride/3 M KOH solution in alkaline fuel cell; cathode: MnO_2 .

3.2. Fuel cell performance

3.2.1. Catalyst type

The j - v characteristics for methanol, ethanol and sodium borohydride fuels with different anode catalysts at a 1 mg cm^{-2} loading are given in Fig. 3a–c. The different anode catalysts tested are Pt-black, Pt/Ru (40 wt.%,20 wt.%) /C and Pt/C (40 wt.% Pt). The performance of the direct methanol and the direct ethanol alkaline fuel cells is slightly higher with the Pt/Ru electrocatalyst. Verma et al. [20] carried out cyclic voltammetry analyses of a half-cell under similar operating conditions, where it was found that Pt/Ru (40 wt.%,20 wt.%) /C gave higher oxidation peaks compared with that of Pt-black in alkaline condition. The results of the cyclic voltammetry substantiated the fuel cell performance data. It is well known that Ru plays a crucial role in the electro-oxidation of methanol and ethanol. Ruthenium is a good CO-tolerant catalyst but not particularly active for methanol or ethanol electro-oxidation. The feature of Ru is to supply OH_{ad} species to aid the oxidation of adsorbed CO and hence enhance the electrocatalytic activity [21]. Thus, the CO formed as a side-reaction is oxidized and the poisoning effect is reduced [22].

The performance of NaBH_4 is little affected for the different anode catalysts tested (Fig. 3c). However, the cell performance for NaBH_4 fuel in the presence of a Pt/C catalyst, however, is slightly lower than that for Pt/Ru and Pt-black-catalysts.

3.2.2. Catalyst loading

In the previous section, it was shown that the Pt–Ru (40 wt.%,20 wt.%) /C catalyst results in slightly higher j - v characteristics compared with Pt-black or Pt/C catalysts. Fig. 4(a–c) shows the j - v characteristics for methanol, ethanol and sodium borohydride fuels at different loadings (0.5 , 1.0 and 1.5 mg cm^{-2}) of Pt/Ru (40 wt.%,20 wt.%) /C. It is seen that the j - v characteristics improve with increase in anode catalyst loading. Beyond a catalyst loading of 1 mg cm^{-2} , however, the j - v characteristics do not improve appreciably for methanol and sodium borohydride fuels while for ethanol the performance improves slightly for a catalyst loading of 1.5 mg cm^{-2} . The anode catalyst layer becomes compacted with increase in catalyst loading for an anode electrode of given size and thickness. This is the reason why no further improvement in j - v characteristics are noticed

beyond 1 mg cm^{-2} of loading. The typical power density achieved when using a Pt–Ru (40 wt. %:20 wt. %)/C catalyst is 15.8 mW cm^{-2} at a current density of 26.5 mA cm^{-2} for methanol and 16 mW cm^{-2} at 26 mA cm^{-2} for ethanol. The typical power density achieved for NaBH_4 is 20 mW cm^{-2} at 30 mA cm^{-2} using Pt-black. The j - v curve for variation of the Pt-black anode catalyst for NaBH_4 is shown in Fig. 4d. A similar trend has been found for a Pt/C a Pt-black anode catalyst for methanol, ethanol and sodium borohydride (not shown).

4. Conclusions

A direct alkaline fuel cell has been constructed with a Pt-black, a Pt/C (40 wt. %) or a Pt/Ru (40 wt. %:20 wt. %)/C as the anode catalyst, MnO_2 as the cathode catalyst, and KOH as the electrolyte. The electrodes are constructed using a catalyst slurry, which is spread on carbon paper with a paint-brush technique. Nickel mesh is used as the current-collector at the electrodes. The alkaline fuel cell fabricated with above electrodes for the direct use of methanol or ethanol or sodium borohydride fuel has been tested and the j - v characteristic curves generated by varying the catalyst and its loading at the anode. The Pt/Ru (40 wt. %:20 wt. %) catalyst produces the best performance for the direct methanol and ethanol alkaline fuel cell. The performance of the direct sodium borohydride fuel cell does not depend on the three different anode catalyst tested. The fuel cell performance improves with increase in anode catalyst loading however, but beyond a catalyst loading of 1 mg cm^{-2} the performance does not increase appreciably except in case of ethanol for which the performance improves slightly using Pt–Ru/C for 1.5 mg cm^{-2} of catalyst loading. The typical power density achieved using the Pt–Ru/C catalyst is 15.8 mW cm^{-2} at a current density of 26.5 mA cm^{-2} for methanol and 16 mW cm^{-2} at 26 mA cm^{-2} for ethanol. The typical power density achieved for NaBH_4 is 20 mW cm^{-2} at 30 mA cm^{-2} using Pt-black.

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