

Short communication

# Alkaline fuel cell: carbon nanobeads coated with metal catalyst over porous ceramic for hydrogen electrode

A.K. Chatterjee<sup>a</sup>, Maheshwar Sharon<sup>b,\*</sup>, Rangan Banerjee<sup>a</sup>

<sup>a</sup>Energy Systems Engineering, Indian Institute of Technology-Bombay, Powai, Mumbai 400076, India

<sup>b</sup>Department of Chemistry, Indian Institute of Technology-Bombay, Powai, Mumbai 400076, India

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## Abstract

The development of a hydrogen electrode using a porous ceramic coated with carbon nanobeads for an alkaline fuel cell (AFC) is reported. This electrode can provide necessary strength and porosity to enable hydrogen to diffuse without allowing electrolyte to percolate inside the electrode. Various catalysts (Pt, Ni, Co and Fe) are electrochemically dispersed over the carbon nanobeads to examine their performance in the alkaline fuel cell. Turpentine oil has been used as a precursor for preparing the carbon nanobeads by a chemical vapour deposition technique. Scanning electron microscopic and transmission electron microscopic images show that the carbon nanobeads have sizes between 500 and 650 nm and are spread uniformly over the entire ceramic substrate. X-ray diffraction (XRD) patterns indicate that the nanobeads are graphitic in nature. Thus, the electrode is highly conductive. The current–voltage characteristics and chronopotentiometry of a half cell (i.e. hydrogen electrode coated with different electrocatalysts) and a full cell (using both hydrogen and oxygen electrodes) with 30% KOH solution are measured. About 93% of the theoretical hydrogen dissociation voltage is obtained with Ni and Pt catalyst. All other metals (Co and Fe) give a lower voltage. Ni-coated carbon nanobeads deposited over a ceramic oxide can be used in place of Raney nickel electrode as their characteristics are similar to those of a platinum electrode.

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## 1. Introduction

The alkaline fuel cell (AFC) is attractive due to its high efficiency, good performance and reliability. AFC electrodes have been prepared from non-noble metal catalysts [1–3]. The Raney nickel electrode uses a metal screen (Ni or Cu), on to which a mixture of electrocatalyst with PTFE is pressed. Although PTFE increases the mechanical strength, water formation during the reduction process results in the generation of local pressure which damages the PTFE film [4]. In order to increase the strength, excess PTFE is added. This makes the electrode completely hydrophobic and prevents flooding of the agglomerates [2,4]. The Raney nickel electrode has a high adsorption ability for hydrogen as well as a relatively large surface area, but is highly resistant to the diffusion of hydrogen and thus restricts the Faradaic efficiency of the cell [5]. Raney nickel is highly reactive and thus must be handled in an inert environment. Thus, though

Raney nickel has been able to eliminate the use of expensive platinum, it has created a fresh set of problems. Highly conductive carbon materials with evenly dispersed electrocatalysts can eliminate these difficulties, provided a method is found to increase the porosity of the carbon. It is possible to make highly porous carbon electrodes but the cost is high. Hence, there is a need to develop an economical process where the problem of carbon porosity can be solved without losing the electrochemical characteristics of the metal catalyst. In order to develop an AFC electrode which has good porosity, low resistivity, mechanical stability and high electroactivity, a new approach is proposed in this study.

Sharon et al. [6] has observed that conducting carbon nanomaterials can be deposited over a non-conducting ceramic oxide substrate such as alumina. Alumina provides the strength and the carbon coating provides the conductivity. Given this approach, it may be possible to use a porous ceramic oxide and deposit a conducting carbon material so that pores of the ceramic oxide become conducting. If this can be achieved, then it may also be possible to deposit electrochemically a desired amount of metal catalyst over

\* Corresponding author. Tel.: +91-22-2576-7174;  
fax: +91-22-2576-7152.  
E-mail address: [sharon@chem.iitb.ac.in](mailto:sharon@chem.iitb.ac.in) (M. Sharon).

these carbon-coated pores. This type of composite can then be used as an electrode for an AFC.

Carbon material can be made with different morphologies, e.g. nanotubes, fibres, and nanobeads. Each of these forms may have an influence on the catalytic properties of the deposited metal. Carbon nanobeads can be obtained by different synthetic methods [7,8]. Depending on the conditions of preparation, the nanobeads differ in size, morphology and porosity. Sharon et al. [9] have obtained carbon nanobeads with a spongy surface from camphor. Turpentine oil is a precursor of camphor and is much cheaper. Hence, as an extension to the work of Sharon et al. turpentine oil is used in this study as a precursor for carbon nanobeads. Moreover, Pt, Ni, Co and Fe have been used as electrocatalysts to ascertain whether platinum can be replaced by other cheap metals. Thus, efforts are also made to evaluate the comparative catalytic activity for hydrogen oxidation with these catalysts.

## 2. Experimental

The chemical vapour deposition unit consisted of two furnaces. One long quartz tube was inserted in both furnaces which were placed side-by-side (Fig. 1). The first furnace was used to vaporise turpentine oil and the other furnace was used to pyrolyze the resulting vapour. Two millilitres of turpentine oil in a quartz boat was placed in the first furnace. Temperature of this furnace was maintained at 250 °C, while that of the second furnace, which contained the ceramic substrate, was maintained at 1000 °C. Argon gas carried the vapour of the turpentine oil from the first to the second furnace for pyrolysis. Pyrolyzed carbon was deposited over the ceramic substrate. The deposition was carried out under a flow of argon for 1 h. After deposition, the furnaces were cooled down and the ceramic substrate coated with carbon was analysed by X-ray diffraction (XRD, Philips-1790) and scanning electron microscopy (JEOL JSM-840). Visual inspection of the ceramic substrate suggested that the carbon was evenly deposited, even in the pores. Electrocatalyst particles were electroplated separately over these carbon beads by applying methods which are discussed elsewhere [10,11]. For platinum deposition,  $\text{H}_2\text{PtCl}_6$  (0.1 M) solution was used. All other metals (Ni, Co and Fe) were electroplated from their nitrate solutions. The carbon powder was

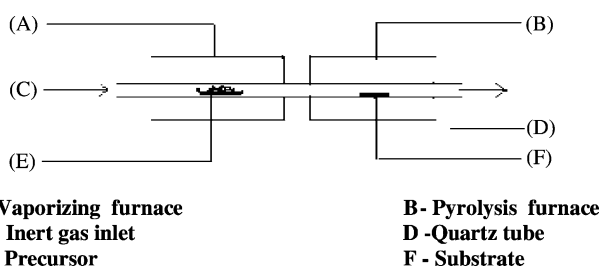


Fig. 1. Schematic of chemical vapour deposition apparatus.

also characterised by transmission electron microscopy (Philips CM-200). The presence of metal catalyst deposited over the carbon nanobeads was also confirmed by X-ray fluorescence. In order to obtain the XRD pattern for the carbon thin film deposited over the ceramic substrate (Fig. 2), the XRD pattern for the ceramic substrate was subtracted from that for the ceramic substrate deposited with the carbon thin film. The ceramic substrate coated with carbon thin films and deposited with electrocatalyst is hereafter is referred to as the ‘hydrogen electrode’. The resistivity of this electrode was measured by the Van der-Pauw method between room temperature and 300 °C in an argon atmosphere (Fig. 3). The electrochemical performance of the hydrogen electrode was studied by fabricating a half cell with the configuration: ‘hydrogen electrode,  $\text{H}_2$ |30% KOH|saturated calomel electrode (SCE)|Pt’. Current–voltage and chronopotentiometric measurements were also conducted on a fuel cell with the configuration: ‘hydrogen electrode,  $\text{H}_2$ |30% KOH|oxygen electrode’.

All electrochemical measurements were performed with a Pine potentiostat, model AFRDE4. The same flow rate of hydrogen (and oxygen for full cell) was maintained in all experiments. The hydrogen dissociation voltage and half cell characteristics were measured using a calomel electrode as the reference electrode, platinum as the counter electrode, and the hydrogen electrode as the working electrode. For full cells, a silver-deposited carbon nanobeads electrode (prepared by a similar process) was used as the positive electrode and a hydrogen electrode as the working electrode.

## 3. Results and discussion

Scanning electron micrographs (Fig. 4) show the presence of carbon nanobeads which have grown over the ceramic support. The nanobeads are highly dense and interconnected. Transmission electron micrographs (Fig. 5) confirm this structure. The nanobeads have diameters in the range 500–650 nm, and their internal structure is similar to that reported by Sharon et al. [10], namely, non-graphitic carbon inside a graphitic shell. The nanobeads are interconnected with graphitic layers which engulf many of the nanobeads. X-ray diffraction patterns (Fig. 2) of the nanobeads show characteristic graphitic peaks ( $2\theta$  value) for the (0 0 2), (1 0 1) and (0 0 4) planes. The hydrogen electrode coated with platinum shows characteristic peaks for Pt (Fig. 2a) at 39.39° (1 1 1), 68.02° (2 2 0) and 81.16° (3 1 1). Likewise, the hydrogen electrode coated with nickel shows characteristic peaks for Ni (1 1 1) and (2 0 0) planes (Fig. 2c), the cobalt-coated hydrogen electrode for cobalt (1 1 1), (2 2 0) planes, and the iron-coated electrode shows iron peaks at 39.94° (1 1 0) and 68.34° (2 0 0). It is interesting to note that, except for cobalt, all the other catalysts (Pt, Ni and Fe) do not have any impact on the growth of the graphitic plane (0 0 2). This suggests that cobalt suppresses the growth of the graphitic (1 0 0) plane at the expense of the (0 0 4) plane.

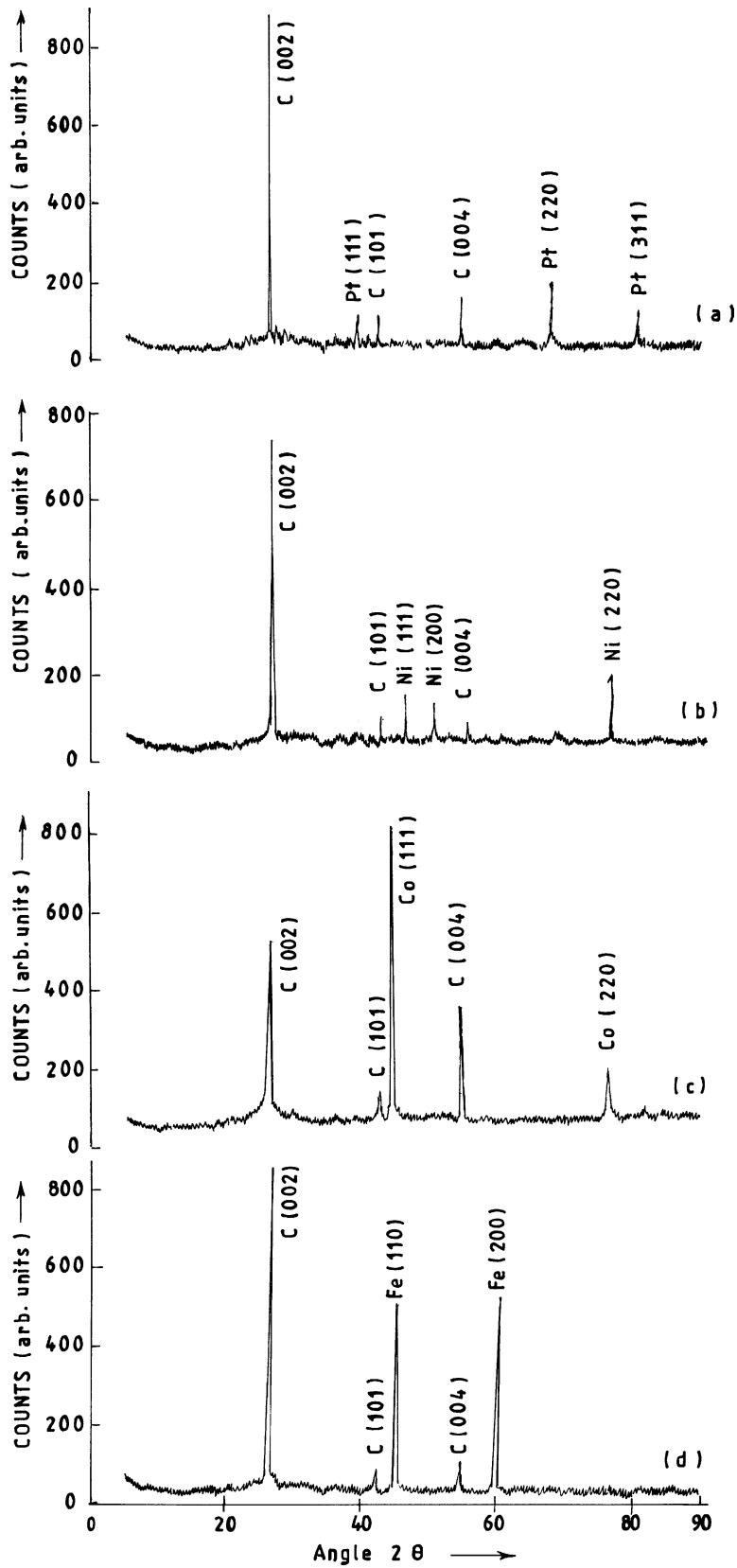


Fig. 2. X-ray diffraction pattern for carbon nanobeads electrodes coated with: (a) Pt; (b) Ni; (c) Co; (d) Fe.

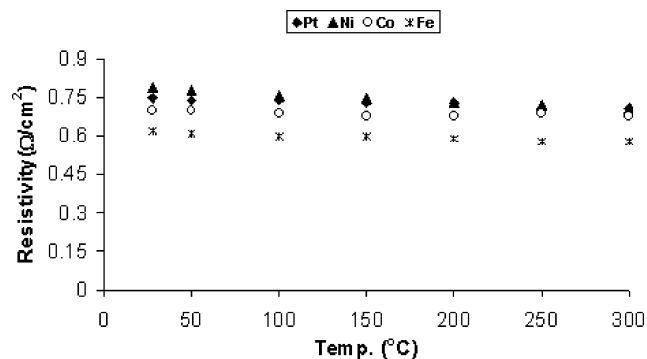


Fig. 3. Variation of sheet resistivity of ceramic electrode coated with carbon nanobeads and metal with temperature.

The presence of Pt, Ni, Co and Fe in the respective hydrogen electrodes was also confirmed by X-ray fluorescence analysis. The variation in the sheet resistivity of carbon nanobead electrodes coated with various metals suggests that deposition of metal does not effect the semi-conducting properties of the carbon nanobeads.

The hydrogen dissociation potential with respect to a saturated calomel electrode in 30% KOH solution for the different carbon nanobead electrodes are summarised in Table 1. The theoretical dissociation potential of H<sub>2</sub> in

Table 1  
Hydrogen dissociation potential vs. SCE

Electrode	Voltage (mV)
Carbon beads + Pt	–998
Carbon beads + Ni	–956
Carbon beads + Co	–756
Carbon beads + Fe	–738

30% KOH solution is  $-1.058$  V [12,13]. The electrodes with Ni or Pt give hydrogen dissociation potential close to the theoretical value (almost 93%), whereas the electrode with iron gives the lowest value. In other words, the catalytic activity of iron for hydrogen dissociation is the least. Since the hydrogen dissociation potential with a ceramic substrate deposited with carbon nanobeads and Ni is almost same as that with platinum, it appears that nickel can be used instead of expensive Pt. The current–potential characteristics and chronopotentiometric data for a half cell (i.e. H<sub>2</sub> electrode only) at 0.2 V for the different electrodes are shown in Figs. 6 and 7, respectively. Since the theoretical values of the hydrogen dissociation potential and the oxygen reduction potential are  $-1.058$  and  $0.17$  V in 30% KOH, respectively, the current–potential characteristics were measured in the range from  $-1.2$  to  $0.2$  V. For Pt and Ni, a high current density

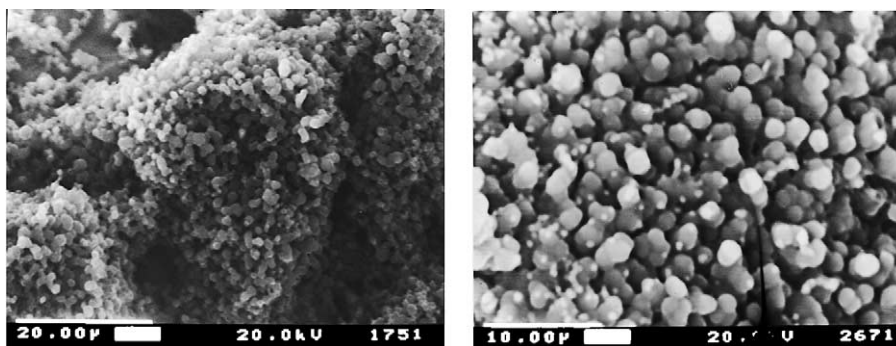


Fig. 4. Scanning electron micrographs of carbon nanobeads.

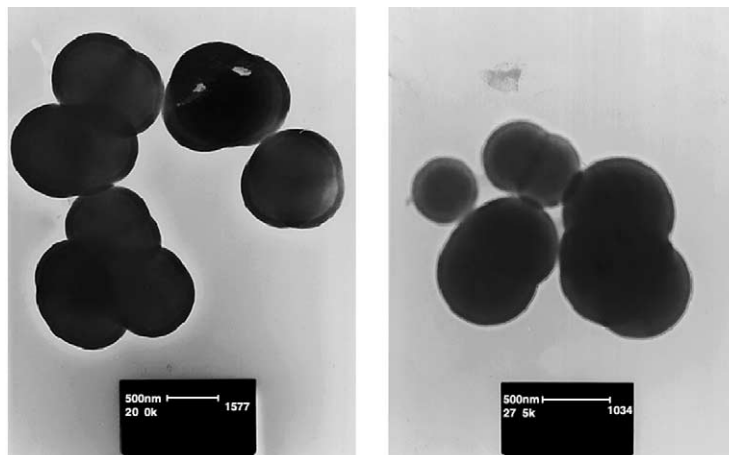


Fig. 5. Transmission electron micrographs of carbon nanobeads.

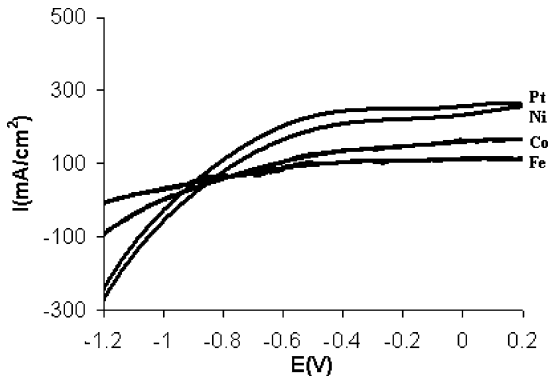


Fig. 6. Current–potential characteristics of hydrogen electrodes coated with various metals in 30% KOH solution saturated calomel electrode used as a reference electrode.

of about 272 and 260 mA cm<sup>-2</sup>, respectively, were observed. The Fe and Co electrodes gave lower current densities of 167 and 113 mA cm<sup>-2</sup>, respectively. The performance of the Pt and Ni electrodes was better than that of the Fe and

Co counterparts due to their better catalytic properties for hydrogen oxidation. The chronopotentiometric data suggest that the Pt and Ni electrodes are more stable in 30% alkaline solution than the Co and Fe electrodes. The data also suggests that hydrogen electrodes coated with Pt or Ni have almost the same characteristics for hydrogen dissociation with a maximum current density of 157 and 148 mA cm<sup>-2</sup>, respectively.

The current–voltage characteristics of an alkaline fuel cell using a hydrogen electrode with an oxygen electrode at scan rate of 50 mV s<sup>-1</sup> are shown in Fig. 8. Again, Pt or Ni electrodes give the highest current densities. Chronopotentiometric data at 0.9 V were recorded for 2 h (Fig. 9) for all the electrodes. The hydrogen electrodes coated with Pt or Ni gave a constant current of 170.12 or 168.01 mA cm<sup>-2</sup>, respectively. By contrast, the electrodes coated with Co and Fe gave very low currents. Thus, Co and Fe are not efficient catalysts for AFC gas-diffusion electrodes. To investigate the chemical stability, the fuel cell was allowed to run for about 8000 s in 30% KOH solution (Fig. 9). The

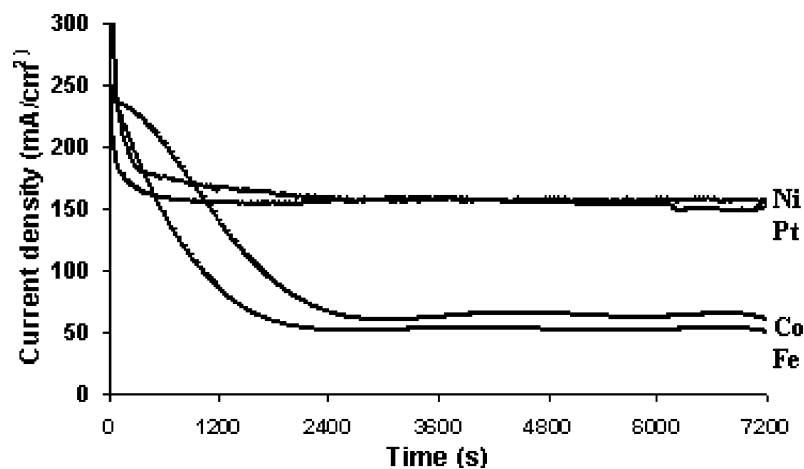


Fig. 7. Chronopotentiometric curves at 0.2 V for hydrogen electrodes coated with various metals.

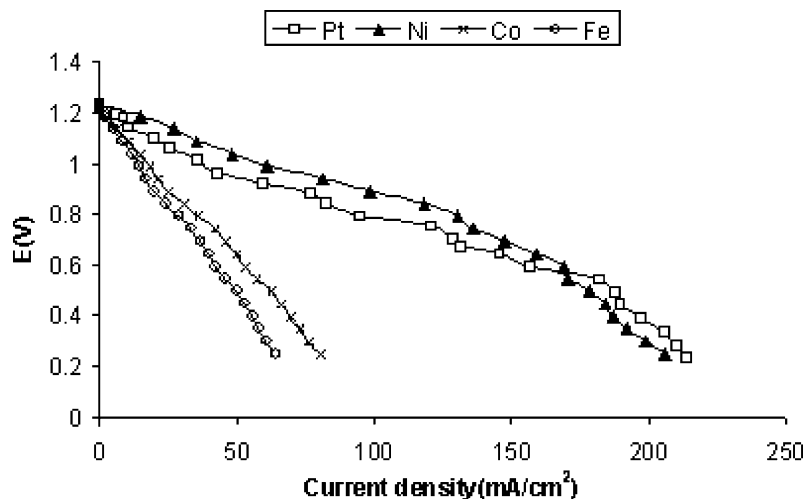


Fig. 8. Full cell current–voltage curves at a scan rate of 50 mV s<sup>-1</sup> for an alkaline fuel cell using hydrogen electrodes with different metals and an oxygen electrode coated with silver.

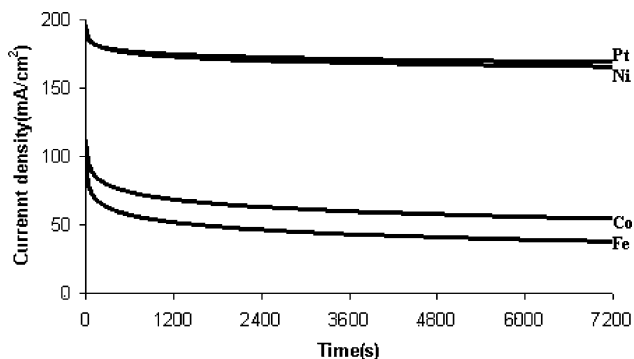


Fig. 9. Full cell chronopotentiometric curves at 0.9 V for an alkaline fuel cell using hydrogen electrodes with different metals and an oxygen electrode coated with silver.

results show that fuel cells using hydrogen electrodes coated with Pt or Ni display almost same behaviour, whereas fuel cells with Co or Fe have poor stability.

#### 4. Conclusions

Metal-coated carbon nanobeads on a porous ceramic are promising options for fuel cell electrodes. The ceramic substrate provides strength to the electrode as well as porosity for good diffusion of the fuel/oxidant. Apart from an ability to assist in electron transportation, the nanobeads can be electroplated with metal particles to provide good activation of the gaseous species. In a novel process, the nanobeads are prepared from turpentine oil, a renewable low cost precursor. From the chronopotentiometric studies, current–voltage characteristics and measurements of the  $H_2$  dissociation voltage, it is obvious that electrodes with Ni-coated carbon nanobeads yield high current densities. This suggests that Ni-coated carbon nanobeads deposited

over ceramic oxide, which has similar characteristics to the platinum electrode, can be used in place of the Raney nickel electrode in alkaline fuel cells.

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