# GLYCEROL-POTASSIUM PERMANGANATE FUEL CELL
# A PRELIMINARY REPORT

**J.S. Banait and Kanwal Nain**

*Chemistry Department, Punjabi University, Patiala - 147 002*

Reaction between glycerol and potassium permanganate has been carried out electrochemically in a H-type cell using different electrodes in both acid and alkaline media and the resulting current measured. The reaction occurs faster in acidic medium as compared to that in alkaline medium. Problems of auto-decomposition of potassium permanganate and corrosion in strong sulphuric acid are discussed. It has been observed that the cell works satisfactorily with commercial sheet type stainless steel as cathode and wrought iron as anode even in the absence of any catalyst.

Fuel cells, when used as combined heat and power generators, exhibit very high overall efficiency [1,3]. However, the catalysts and the other materials are generally very expensive, and they are eaten up after some time due to the corrosive nature of electrolytes and thus add significantly to the cost of the production of electricity. In countries like India where the by-product heat cannot be used by local domestic consumers (due to the hot weather), the production cost increases further. Efforts, have, therefore, been made to study a fuel cell which can work at room temperature with cheep electrodes.

## EXPERIMENTAL

H-type cell with two sintered discs of G-3 was fabricated from Pyrex glass (Fig.1). Solution of sulfuric acid/sodium hydroxide of required strength were prepared. Solutions of glycerol 5% in the acid/alkali solution was taken in A and 5% solution of potassium permanganate was taken in C compartments (Fig. 1). Acid/alkali solution was taken in the central compartment. The solutions in the three compartments were kept at the same level. Electrodes of the appropriate metals were dipped in the compartments A and C. The current produced and voltage with out and with added load were measured using different combinations of electrodes.

Strips of zinc, cobalt, nickel, iron, and tin-all of specpure grade - were obtained from Johnson Matthey Chemicals Ltd., England. Perforated gauze type platinum electrodes were used. A thick layer of copper was deposited electrochemically on a strip of copper and was then used as electrode. A strip from the

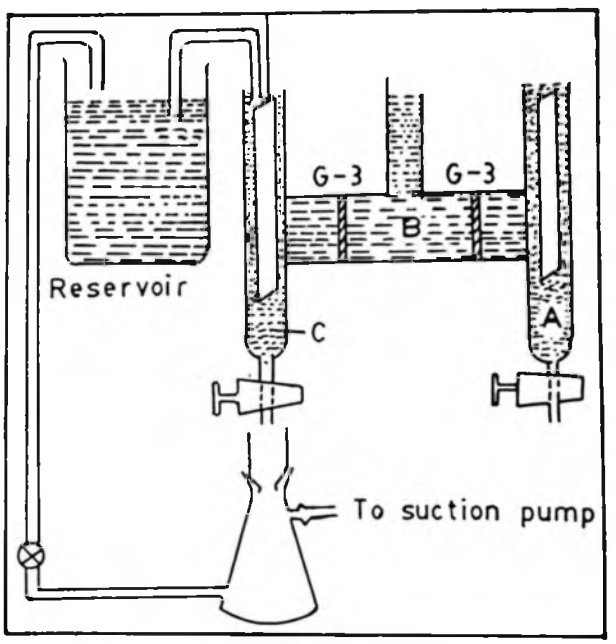



Fig. 1 The Fuel Cell Set Up

stainless steel (sheet type) used for the manufacture of domestic utensils and a small piece from the iron rods used in the construction of buildings were also used as electrodes.

The compartments A and C were provided with stop-cocks at the base. The solution from C of the cell was freed from manganese dioxide by filteration and pumped to reservoir. The solution from reservoir enters the cell through syphen so that there is a continuous flow of potassium permanganate solution.



0013 466 x 37 (36) 249-254

Further additions of potassium permanganate to the solution was made in the reservoir.

## RESULTS AND DISCUSSION

### Reaction in Acidic Medium

Preliminary studies, with different electrodes at different temperatures have shown no significant effect on the current produced with the rise in temperature. Therefore, all the measurements have been carried out at room temperature. All the relevant data are summarized in Table 1.

Table 1 shows that the best performance is at platinum cathode. Of the baser metals, steel-nickel, steel-iron, steel-tin, cobalt-nickel, cobalt-carbon, cobalt-steel, nickel-carbon, nickel-iron, tin-nickel, tin-carbon, tin-copper, iron-carbon, copper-nickel, etc, give good currents.

In acid medium, permanganate is reduced to Mn (II) and in alkaline medium to $MnO_2$. However when the cell is working for a few hours, $MnO_2$ separates even in acid medium. This is because $Mn^{2+}$ formed in acid medium reacts with $MnO_4^-$ as follows.

$$2\ MnO_4^- + 3\ Mn^{2+} + 2H_2O \longrightarrow 5\ MnO_2 + 4\ H^+ \quad ..(1)$$

The presence of $MnO_2$ in permanganate solution is considered to be highly objectionable because it catalyses auto decomposition of potassium permanganate [4] solutions.

$$4\ MnO_4^- + 2\ H_2O \longrightarrow 4\ MnO_2 + 3\ O_2 + 4\ OH^- \quad ..(2)$$

In the present studies, it has been observed that the cell gives rise to oxygen evolution after working the cell for about 10 hours.

As the reaction (1) is slow is acidic nedium, stronger acids have been used to minimise the precipitation of $MnO_2$ However this conversion is observed to some extent even in 18 N $H_2SO_4$

As the permanganate decomposition is catalysed by $MnO_2$ , the precipitated $MnO_2$ is removed continuously from the cathode solution and the concentration of permanganate is maintained constant by suitable additions (Fig 1).

Nickel, iron, cobalt and copper as anode has been checked with stainless steel cathode in 18 N sulphuric acid for periods varying from

TABLE 1

CURRENT PRODUCED WITH DIFFERENT COMBINATIONS OF THE ELECTRODES IN DIFFERENT CONCENTRATIONS OF SULFURIC ACID

| Anode | Cathode | Current produced (mA) in acid concentration of | | |
|---|---|---|---|---|
| | | 2 N | 4 N | 6 N |
| Carbon | Platinum | 0.6 | 3.2 | - |
| Iron | " | 80.0 | >100 | >100 |
| Cobalt | " | 89.0 | " | " |
| Tin | " | 90.00 | " | " |
| Nickel | " | 58.0 | 93.0 | 95.0 |
| Copper | " | 53.00 | 74.0 | 87.5 |
| Steel | " | 9.0 | 7.3 | 14.0 |
| Platinum | Tin | 7.0 | 8.0 | 8.2 |
| " | Iron | 3.7 | 6.5 | 0.4 |
| " | Cobalt | 3.7 | 2.2 | 5.3 |
| " | Copper | 0.3 | 0.6 | 0.3 |
| " | Steel | 1.4 | 0.2 | 0.7 |
| " | Nickel | 2.0 | 0.2 | 0.3 |
| " | Carbon | 2.8 | 1.1 | - |
| Nickel | Tin | 1.5 | 0.5 | 3.2 |
| Iron | " | 0.6 | 2.6 | 2.8 |
| Cobalt | " | 0.0 | 0.8 | 2.7 |
| Copper | " | 5.1 | 0.3 | 1.1 |
| Steel | " | 1.2 | 1.7 | 4.5 |
| Carbon | " | 1.0 | 1.2 | - |
| Tin | Nickel | 70.5 | 83.5 | 97.0 |
| " | Iron | 14.5 | 20.0 | 16.5 |
| " | Cobalt | 2.05 | 2.8 | 9.0 |
| " | Copper | 27.0 | 39.0 | 40.0 |
| " | Steel | 54.0 | 68.0 | 17.0 |
| " | Carbon | 37.5 | 40.0 | - |
| Nickel | Cobalt | 1.0 | 1.9 | 1.4 |
| " | Copper | 1.6 | 0.5 | 1.6 |
| " | Steel | 33.5 | 35.0 | 39.0 |
| " | Carbon | 54.0 | 15.0 | - |
| " | Iron | 0.7 | 1.5 | 0.6 |
| Cobalt | Nickel | 66.5 | 60.0 | 85.0 |
| Copper | " | 33.0 | 56.0 | 67.0 |
| Steel | " | 2.3 | 1.4 | 1.0 |
| Carbon | " | 3.0 | 1.0 | - |
| Iron | " | 58.5 | 77.5 | 79.5 |
| Cobalt | Copper | 23.0 | 37.5 | 16.0 |
| " | Carbon | 70.0 | >100 | - |
| " | Iron | 7.5 | 5.8 | 8.0 |
| Copper | Coblat | 1.0 | 0.9 | 4.8 |
| Steel | " | 1.1 | 1.4 | 0.4 |
| Carbon | " | 1.5 | 2.0 | - |
| Iron | " | 3.7 | 3.7 | 6.0 |
| Iron | Copper | 14.5 | 20.0 | 3.2 |
| " | Steel | 37.5 | 49.5 | 15.5 |
| " | Carbon | 62.5 | 88.0 | - |
| Copper | Iron | 2.4 | 6.0 | 1.2 |
| Steel | " | 0.1 | 0.2 | 0 |
| Carbon | " | 0 | 6.7 | - |
| Copper | Steel | 27.5 | 20.5 | 7.0 |
| Steel | Copper | 0 | 0.5 | 0.1 |

15 hours to 20 hours (Table 2). The currents are high but the extenst of corrosion also in high.

In this study, electrodes of 12 $cm^2$ area are used normally. However the effect of varying surface area also is studied (Table 3). This table shows that current increases with area, but the increase is not proportional. In this cell, the electrolyte is highly conducting but interelectrode distance large and there are two sintered discs between them. The resistance of the cell is measured and found to be 15 $\Omega$. This is very high for a fuel cell. The less than linear variation of current with area is attributed to the higher internal resistance. The variation of cell voltage and current with external load (Table 4) also conform the effect of large internal resistance.

It has been observed that the stainless steel and wrought iron electrode pair gives a fairly good value of the current density. However corrosion of anode material is high.

TABLE 2

WORKING OF THE CELL IN 18 N $H_2SO_4$ WITH TIME USING STEEL CATHODE

| Anode | Average current in mA after 10 | 15 | 20 hrs |
|---|---|---|---|
| Nickel | 55.0 | 30.0 | 27.3 | 26.2 |
| Iron | 53.2 | 52.2 | 50.1 | - |
| Copper | 41.2 | 40.0 | 38.4 | - |
| Cobalt | 48.6 | 27.3 | 46.2 | - |

TABLE 3

EFFECT OF SURFACE AREA OF ELECTRODES

| Current (mA) with electrode of area 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 $cm^2$ |
|---|---|---|---|---|---|---|---|
| Medium 12 N acid; Co anode of 12 $cm^2$ ; Cathode area varying | | | | | | | |
| 45 | 49 | 53 | 56 | 60 | 64 | - | - |
| Medium 12 N acid; Steel Cathode of 12 $cm^2$ ; Co anode area varying | | | | | | | |
| 54 | 56 | 59 | 61 | 65 | 66 | - | - |
| Medium 18 N acid; Steel Cathode of 12 $cm^2$ ; Iron anode area varying | | | | | | | |
| 43 | 46 | 48 | 53 | 56 | 57.5 | 57.5 | 59 |
| Medium 18 N acid; Iron anode of area 16 $cm^2$ ; Steel cathode area varying | | | | | | | |
| 45 | 48 | 50 | 53 | 55 | 58 | - | - |
| Medium 18 N acid; area of both iron anode and steel cathode varying | | | | | | | |
| 35 | 40.5 | 45 | 49.5 | 5.3 | 5.5 | - | - |

TABLE 4

CURRENT AND VOLTAGE OF THE CELL AT DIFFERENT EXTERNAL LOAD
Area of the electrodes 12 $cm^2$

| Load (ohms) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Cobalt anode: Steel cathode | | | | | | | | |
| Voltage (V) | 0.2 | 0.25 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| AV-current (mA) | 57.5 | 55.5 | 53.5 | 47.5 | 39.5 | 34.0 | 32.0 | 30.0 |
| Copper anode: Steel cathode | | | | | | | | |
| Voltage (V) | 0.15 | 0.2 | 0.2 | 0.25 | 0.3 | 0.3 | 0.35 | 0.4 |
| AV-current (mA) | 60.0 | 52.0 | 45.5 | 42.5 | 40.5 | 39.0 | 37.0 | 35.0 |
| Nickel anode: Steel cathode | | | | | | | | |
| Voltage (V) | 0.2 | 0.25 | 0.3 | 0.35 | 0.4 | 0.4 | 0.45 | 0.5 |
| AV-current (mA) | 67.5 | 63.5 | 61.0 | 61.0 | 58.5 | 52.0 | 44.5 | 37.5 |

TABLE 5

CONSUMPTION OF THE REACTANTS AND ELECTRODES IN 18 N SULFURIC ACID; CATHODE STEEL

| Anode | Time (hrs) | Weight loss (mg/$cm^2$ /hr) Cathode | Anode | $KMnO_4$ used(g) | Glycerol used (ml) |
|---|---|---|---|---|---|
| Cobalt | 15 | 0.5 | 7.3 | 15 | 20 |
| Iron | 15 | 0.5 | 3.7 | 15 | 20 |
| Nickel | 21 | 0.5 | 2.1 | 23 | 25 |
| Copper | 15 | 0.6 | 3.5 | 15 | 20 |
| Wrought iron | 114 | 0.6 | 20.4 | 110 | 30* |

* 25.59 g of $MnO_2$ is formed

But the electrodes, commercial sheet type stainless steel (used for manufacturing domestic utensils) as cathode and wrought iron rod (a small piece from the iron rod used in the construction of buildings) as anode, are quite cheap. Though the weight loss of this anode is comparatively more, it still gives the cheapest cell because of the low electrode cost. Weight loss of the electrodes, potassium permanganate and glycerine used and manganese dioxide produced are recorded in Table 5.

It has been observed that the current and potential remain almost constant for about 20 hours at a given external load. The internal resistance therefore, changed only after a period of 10-20 hours. Perusal of Table 6 reveals that though there is a continuous increase in the voltage of the cell with the increase in the external load, the effect on current is much less when the resistance is in the range of 4-7 ohms. This may be taken as the optimum external load at which the cell works.

Working of the cell has also been studied by keeping the applied load constant (4 ohms) for a period of 60 hours using stainless steel and iron electrodes. It has been observed that the variation in current (58-61 mA) and potential (0.34-0.35 V) is almost negligible during the whole period.

It has been observed that a continuous circulation of potassium permanganate solution is very important in the working of this cell.

TABLE 6

WORKING OF THE CELL USING STAINLESS STEEL CATHODE AND WROUGHT IRON ANODE IN 18 N SULFURIC ACID

| Time hrs | Average current (mA) | Applied load (ohm) | Potential (Volt) |
|---|---|---|---|
| 10 | 75.5 | 1 | 0.15 |
| 20 | 72.0 | 1 | 0.2 |
| 30 | 70.3 | 2 | 0.25 |
| 40 | 69.4 | 2 | 0.25 |
| 50 | 62.2 | 3 | 0.3 |
| 60 | 59.1 | 4 | 0.35 |
| 70 | 58.0 | 5 | 0.4 |
| 80 | 57.3 | 6 | 0.45 |
| 90 | 56.5 | 7 | 0.5 |
| 100 | 55.5 | 8 | 0.5 |
| 110 | 55.0 | 8 | 0.5 |

If the solution is allowed to stand in the cathode compartment, manganese dioxide is produced which not only enhances the auto-decomposition of potassium permanganate but also decreases the current significantly due to its deposition on the surface of the electrode. In such a case the electrode has to be cleaned.

In the fuel cells which consume organic compounds as fuels [5,9], the organic compounds are either steam reformed to give hydrogen or are used as such at the electrodes. The disadvantages of the latter type of fuel cells are the high cost of the platinum catalyst and the low exchange current densities. Disadvantages of the former type of fuel cells are the less electrical efficiency (as some of the heat is used in the process of steam reforming).

In the present studies, all the chemicals and electrode materials used in the cell are easily available in the market and are also quite cheap. Some of potassium permanganate is wasted due to its auto-decomposition but it can be controlled by efficient circulation process. The circulation process also helps in maintaining the proper concentration of the reactants in the cell.

The by-product of this cell (manganese dioxide) is also an oxidizing reagent and has several applications not only in chemistry laboratory but also in industry. The most common one is in the manufacture of dry cells. Thus marketing of manganese dioxide will not be a problem.

**Reactions in Alkaline Medium**

The electrochemical reaction has been conducted in 2N, 4N and 6N sodium hydroxide solution in the same cell. The open circuit currents with different combinations of the electrodes have been measured and are recorded in Table 7.

Perusal of Table 7 reveals that the currents in alkaline medium are less than in acid; but among alkaline media, the performance of the cell in 4N NaOH solution is better than that in 2N solution. Further, in alkaline medium the performance of tin cathode is best in the combinations studied. The anodes which give high current density with tin cathode are nickel, cobalt, steel, iron and platinum. The other combinations of electrodes which give high current density in alkaline medium are iron-nickel, copper-steel, and copper-

TABLE 7

CURRENT PRODUCED WITH DIFFERENT COMBINATIONS OF THE ELECTRODES IN DIFFERENT CONCENTRATIONS OF SODIUM HYDROXIDE

| Anode | Cathode | Current produced at alkali concentration of | | |
|---|---|---|---|---|
| | | 2N | 4N | 6N |
| Iron | Platinum | 11.5 | 19.5 | 3.0 |
| Cobalt | " | 2.1 | 2.7 | 41.5 |
| Nickel | " | 0.9 | 6.0 | 4.0 |
| Copper | " | 16.0 | 35.5 | 36.5 |
| Steel | " | 0.9 | 5.5 | 5.0 |
| Tin | " | 38.5 | 79.5 | - |
| Platinum | Iron | 10.0 | 2.1 | 2.0 |
| " | Cobalt | 3.5 | 2.0 | 11.0 |
| " | Nickel | 2.6 | 1.7 | 3.0 |
| " | Tin | 3.8 | 0.7 | - |
| " | Copper | 3.3 | 1.8 | 2.0 |
| " | Steel | 5.6 | 4.5 | 6.0 |
| Cobalt | Iron | 5.6 | 1.8 | 26.0 |
| Nickel | " | 5.7 | 6.2 | 13.0 |
| Steel | " | 20.0 | 7.5 | 12.5 |
| Copper | " | 24.0 | 30.0 | 11.0 |
| Tin | " | 58.0 | 72.0 | - |
| Iron | Copper | 18.0 | 13.5 | 2.5 |
| " | Nickel | 4.5 | 11.0 | 27.5 |
| " | Cobalt | 3.8 | 15.0 | 1.0 |
| " | Steel | 4.0 | 16.5 | 1.0 |
| " | Tin | 0.8 | 3.0 | - |
| Nickel | Tin | 1.1 | 1.0 | - |
| " | Steel | 1.4 | 5.6 | 5.0 |
| " | Copper | 0.4 | 3.0 | 20.5 |
| " | Cobalt | 5.2 | 4.5 | 10.5 |
| Tin | Nickel | 55.0 | 72.0 | - |
| Steel | " | 15.0 | 10.0 | 12.5 |
| Copper | " | 13.0 | 38.5 | 37.7 |
| Cobalt | " | 25.0 | 30.0 | 27.0 |
| Tin | Cobalt | 0.7 | 58.5 | - |
| Copper | " | 0.7 | 19.5 | 15.0 |
| Steel | " | 0.6 | 3.2 | 1.0 |
| Cobalt | Tin | 0.7 | 1.0 | - |
| " | Copper | 0.7 | 2.5 | 3.0 |
| " | Steel | 0.6 | 3.3 | 3.5 |
| Copper | Tin | 19.4 | 22.5 | - |
| Steel | " | 3.5 | 2.5 | - |
| Tin | Copper | 26.0 | 55.5 | - |
| " | Steel | 53.0 | 74.5 | - |
| Steel | Copper | 2.6 | 6.5 | 1.0 |
| Copper | Steel | 24.0 | 35.0 | 33.0 |

platinum. It is worth noting that the current density with pt electrode is quite low in alkaline media.

TABLE 8

WORKING OF THE CELL USING STAINLESS STEEL CATHODE AND TIN ANODE IN 4 N SODIUM HYDROXIDE
The Resistance Applied 1.0 Ohm

| Time/Hrs | E/V | i/mA |
|---|---|---|
| 5 | 0.15 | 60.8 |
| 10 | 0.15 | 56.2 |
| 15 | 0.1 | 48.5 |
| 20 | 0.1 | 44.0 |
| 25 | 0.1 | 42.4 |
| 30 | 0.1 | 41.4 |
| 35 | 0.1 | 40.8 |
| 40 | 0.1 | 39.6 |
| 45 | 0.1 | 38.9 |
| 50 | 0.1 | 38.4 |
| 54 | 0.1 | 38.0 |

TABLE 9

CONSUMPTION OF THE REACTANTS AND ELECTRODES IN 4 N SODIUM HYDROXIDE
$KMnO_4$ used 30 g ; Glycerol used 16 ml

| Cathode | Anode | Time (hr) | Weight loss ($mg/cm^2/hr$) Anode | Cathode |
|---|---|---|---|---|
| Steel | Sn | 54 | 4.25 | 0.56 |
| Ni | Cu | 40 | 1.66 | 0.33 |

TABLE 10

WORKING OF THE CELL IN 4 N NaOH USING NICKEL AS CATHODE AND COPPER AS ANODE
load 1 Ω potential 0.15 V

| Time/ hr | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 |
|---|---|---|---|---|---|---|---|---|
| i/mA | 33.6 | 32.2 | 32.0 | 31.0 | 29.5 | 27.3 | 27.2 | 26.7 |

The cell has been studied for 54 hours using steel as cathode and tin as anode. The current produced at various intervals of time is recorded in Table 8. Weight loss of the cathode and anode is also recorded in the Table 9. Perusal of Table 8 and Table 9 reveals that though the performance of the cell with tin anode is quite satisfactory, the dissolution of tin anode is several times more than steel cathode. The cell has, therefore, been tested using nickel cathode and copper anode for 40 hours. The current at different intervals of time is recorded in Table 10. Weight loss of the cathode and anode along

with other relevant data are recorded in Table 9. Corrosion of nickel is significantly less than that of tin.

It has been observed that using both these electrode pairs, no solid manganese dioxide separated out in the cathode compartment. However, the solution becomes highly viscous and the colour also changes from violet to blue. Due to the increase in the viscosity of the solution, the current density decreases significantly.

The current produced by the cell has also been measured by varying the surface area of the electrodes and the external load. The data are listed in Tables 11 and 12. A perusal of Table 11 and Table 12 reveals that in alkaline medium also the variation in current is not as large as expected. This can also be attributed to the high internal resistance of the cell.

Examination of the results of the present studies shows that in acidic medium, the current density is more, the corrosion of the electrode material is comparatively less, the electrodes used are also very cheap and with the continuous removal of manganese dioxide from the reaction mixture, the auto-decomposition of potassium permanganate is reduced significantly and also the cell be used for sufficiently longer periods of time.

TABLE 11

EFFECT OF SURFACE AREA OF THE ELECTRODES ON CURRENT OF THE CELL IN 4N SODIUM HYDROXIDE

| Nickel cathode | Copper Anode | i/(mA) |
|---|---|---|
| 2 | 6 | 11.0 |
| 4 | " | 13.0 |
| 6 | " | 15.5 |
| 8 | " | 22.5 |
| 10 | " | 26.0 |
| 12 | 2 | 27.0 |
| " | 4 | 28.0 |
| " | 6 | 28.5 |

TABLE 12

CURRENT AND POTENTIAL AT DIFFERENT APPLIED LOADS (4N NaOH)

| | Anode Zinc | | | Cathode Ni | | | | |
|---|---|---|---|---|---|---|---|---|
| E/V | 0.15 | 0.2 | 0.25 | 0.3 | 0.35 | 0.35 | 0.4 | 0.45 |
| Load (ohm) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| i/mA | 57.5 | 55.5 | 54.5 | 53.0 | 52.0 | 50.0 | 48.0 | 47.0 |

The reaction between potassium permanganate and glycerol is highly exothermic and takes place just on mixing the two reagents. In order to minimize the mixing of the two reagents and hence the chemical reaction, the three compartment cell has been used in the present studies. But this cell offered very high internal resistance. Survey of literature reveals that in most of the fuel cells ion permeable membranes separate compartments. The resistance offered by these separators is so low that the internal resistance of the cell is almost negligible. The distance between the two electrodes in a cell is also of the order of a centimeter or two. So there is a need to modify the cell to minimise the internal resistance of the cell.

REFERENCES


1. D.S. Cameron, *Platinum Metal Rev.*, **29** (1985) 107.
2. J.P. Ackerman, *Progress in Batteries and Solar Cells*, 5 (1984) 13.
3. G. Wilemski, *ibid*, 5 (1984) 278.
4. A.I. Vogel, *"Quantitative Inorganic Analysis including Elementary Instrumental Analysis"*, **Longmans Green** London (1961).
5. K. Strasser, H. Gruene and B.H. Gutbier, *Power Sources*, **6** (1977) 569-92.
6. M.Yu. Col'f Kouich, *Elektrokhimiya*, **14(3)** (1978) 361-8.
7. F.J. McElory, J.P. Chludzinski and P. Rantowitz, *Ger. Offen.* (1984) 3, 345, 956.
8. H. Kawana, T. Horiba, K. Iwamoto, K. Fujita and K. Tamura, *Eur. Pat. Appl-EP* **68** (1983) 508.
9. J.S. Yao, Jr., K.S. Wolfson, K.R. Rent, W.R. Keller and Y.H. Yao, *Trans. Am. Soc. Artif. Intern. Organs*, **25** (1979) 45-50.