

# Electrocatalysis of Oxygen Reduction on Platinum-Free Cathode Catalysts for Alkaline Membrane Fuel Cells

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## Introduction

Fuel cells operating below 100 °C are very attractive energy conversion technology for automotive applications due to their higher efficiencies and higher peak power density values. Due high cost and limited durability and reliability of the fuel cell components, commercialisation of this technology has not been widely realised as yet. In the cost point of view there is a huge interest in developing fuel cell electrodes with lower amount of noble metal catalysts or non-noble metal catalysts [1,2] towards the oxygen reduction reaction (ORR).

The aim of this work was to study multi-walled carbon nanotube (MWCNT) supported cobalt phthalocyanine (CoPc) and iron phthalocyanine (FePc) electrocatalysts as alternative cathode materials to Pt/C in alkaline membrane fuel cell (AMFC). We have also explored the electrocatalytic activity of FePc/MWCNT and CoPc/MWCNT modified glassy carbon (GC) electrodes towards oxygen reduction using the rotating disk electrode (RDE) method. The fuel cell performance of CoPc and FePc modified MWCNTs was investigated by fabricating membrane-electrode assemblies (MEAs) using Tokuyama membrane (# A201) and compared with unmodified MWCNT and commercial Pt/C catalysts.

## Experimental

The commercial iron (II) phthalocyanine (FePc), cobalt (II) phthalocyanine (CoPc) and multi-walled carbon nanotubes (MWCNTs) were used for the experiments. A mixture of 200 mg FePc or CoPc and 200 mg MWCNTs in 40 ml isopropanol was prepared and sonicated for 30 min followed by magnetic stirring for 1 h. The homogeneous mass was placed in a ceramic boat, vacuum dried at 100 °C and pyrolysed at 800 °C for 2 h in flowing argon atmosphere. The surface composition of the as-received MWCNT, FePc/MWCNT and CoPc/MWCNT materials was analysed using X-ray photoelectron spectroscopy (XPS). For the RDE experiments a GC disk of geometric area of 0.2 cm<sup>2</sup> was used as substrate material. Electrodes were modified with different catalysts using aqueous suspensions (1 mg ml<sup>-1</sup>) containing 0.5% OH<sup>-</sup> ionomer solution. The electrochemical measurements were made using the RDE technique. Electrochemical experiments were carried out in 0.1 M KOH solution at room temperature. Membrane-electrode assemblies (MEAs) were fabricated with commercial carbon-supported Pt catalyst (Pt/C) as anode catalyst and FePc/MWCNT, CoPc/MWCNT and commercial catalyst (Pt/C) on cathode sides of the Tokuyama polymer membrane (A201 membrane, Tokuyama Corporation, Japan). The single cell fuel cell performance was evaluated with humidified (100% RH) H<sub>2</sub> and O<sub>2</sub> gases at 45 °C using Greenlight Test Station. The flow rates were fixed at 200 and 400 SCCM for H<sub>2</sub> and O<sub>2</sub>, respectively.

## Results

### XPS analysis of FePc/MWCNT and CoPc/MWCNT samples

Figure 1 presents the XPS survey spectra of CoPc/MWCNT sample. Four XPS peaks were observed for both samples, which correspond to emission from C1s, satellite peak of the C1s spectrum, O1s and N1s levels. In addition Co2p peak has been detected for CoPc/MWCNT samples. The O1s peak is related to the MWCNT material and is caused by various carbon-oxygen functionalities on the surface of CNTs. Detection of different functional groups from the O1s peak is not straightforward because of similar binding energies. The XPS core-level spectrum in the N1s region of CoPc/MWCNT sample shows two peaks. The peak at 399.8 eV could be assigned to N introduced into the graphene layer but the N1s peak at higher binding energy at 400.2 eV corresponds to a new nitrogen species formed likely during the pyrolysis.

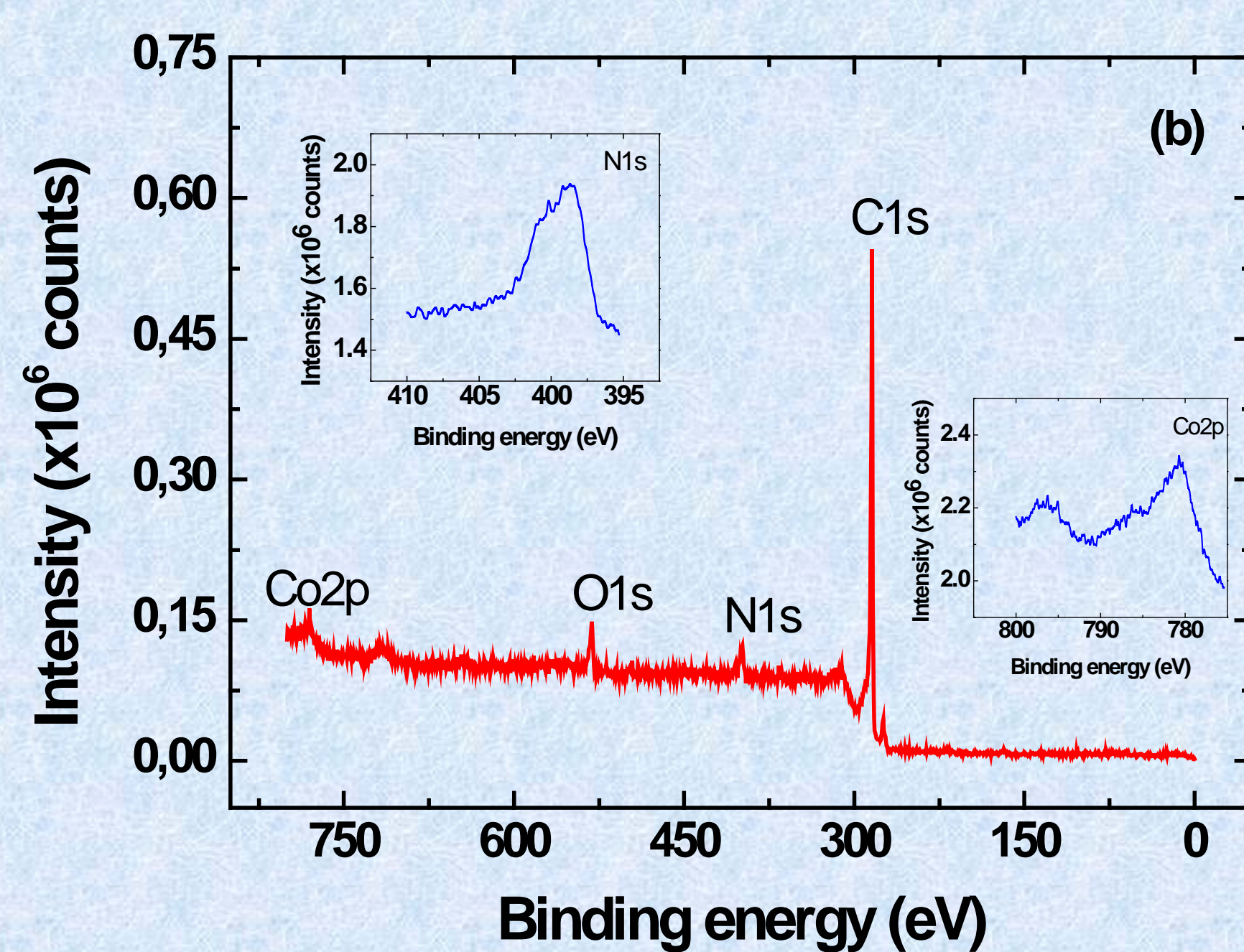


Figure 1. XPS spectra of CoPc/MWCNT catalyst with inset spectra of N1s and Co2p.

### Rotating disk electrode studies of O<sub>2</sub> reduction

A comparison of the RDE data on oxygen reduction recorded on GC electrodes modified with different catalyst materials in O<sub>2</sub> saturated 0.1 M KOH are presented in Figure 2. The commercial catalyst Pt/C 46 wt.% shows a higher reduction current than any other material compared and this is related to the high loading of Pt. At the foot of the polarisation curve the commercial catalyst Pt/C 20 wt.% also shows a higher reduction current than phthalocyanines but at more negative potentials the CoPc/MWCNT modified electrode becomes more active and its current rate exceeds the current values of Pt/C 20 wt.% material. FePc/MWCNT also shows the extraordinary ORR performance in alkaline electrolyte but its current is not rising as high as that observed for the CoPc/MWCNT material. Koutecky-Levich (K-L) analysis of the RDE data on oxygen reduction has been made. The intercepts of the extrapolated K-L lines were close to zero, which shows that the process of O<sub>2</sub> reduction is almost entirely under the diffusion control. It was found that for the CoPc/MWCNT material the value of *n* is close to 3 at -0.4 V but at more negative potentials the *n* value gradually increases and approaches almost four, which indicates that the peroxide formed reduces further to water in this potential range.

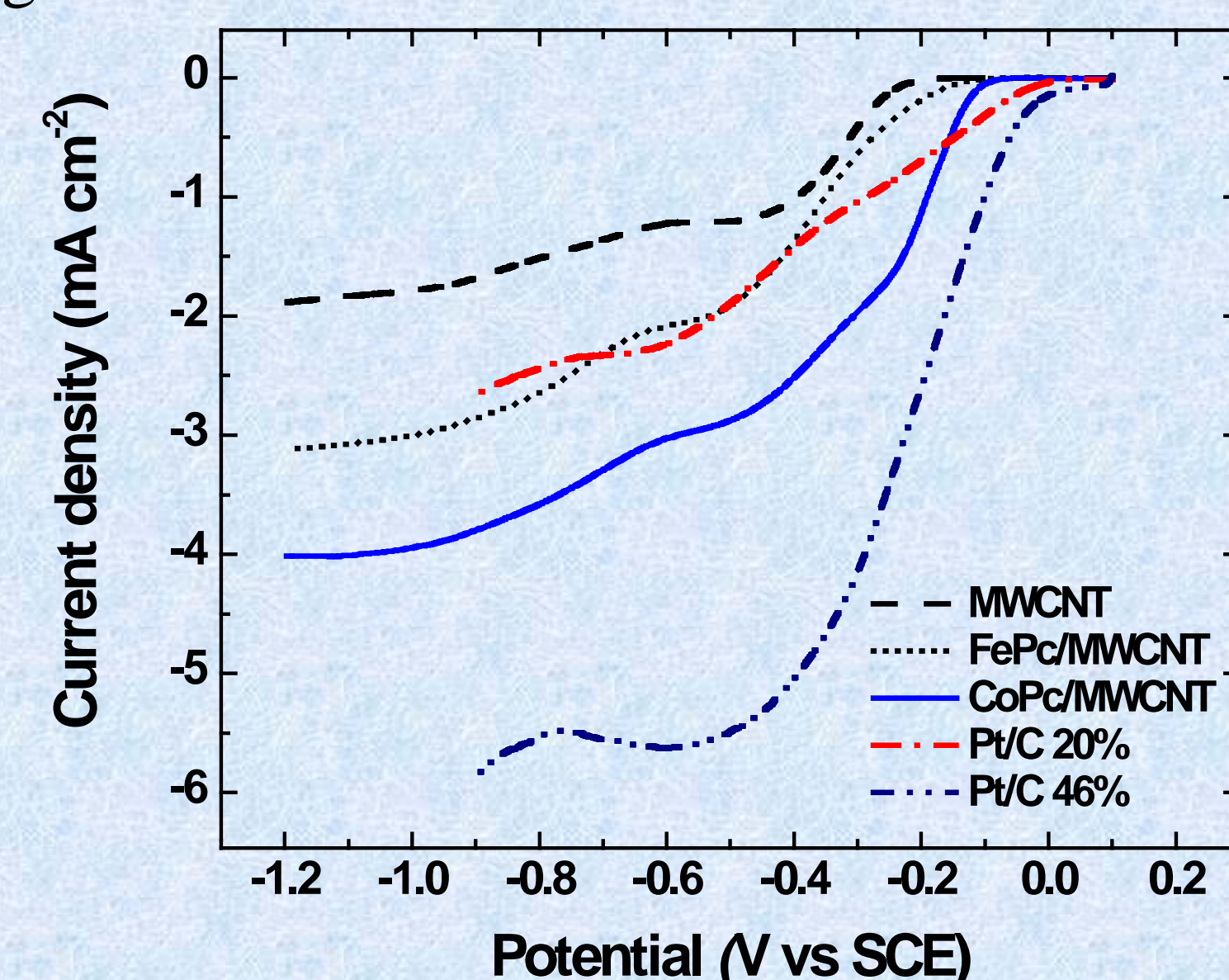


Figure 2. RDE voltammetry curves for oxygen reduction on different catalyst material modified GC electrodes in O<sub>2</sub>-saturated 0.1 M KOH.  $v = 10 \text{ mV s}^{-1}$ .  $\omega = 1900 \text{ rpm}$ .

### Fuel cell performance of FePc/MWCNT and CoPc/MWCNT catalysts

Figure 3 compares the fuel cell performance of MEAs with FePc/MWCNT and CoPc/MWCNT cathode catalysts using humidified H<sub>2</sub> and O<sub>2</sub> gases at 45 °C in a single cell fuel cell. In order to compare the performance of these non-noble metal catalysts, two commercial Pt/C catalysts (E-TEK and Tanaka) were also evaluated and the performance compared at identical operating conditions. As can be seen from the Figure, Tanaka Pt/C catalyst showed the highest performance (~ 120 mW cm<sup>-2</sup>). CoPc/MWCNT performed almost (power density ~ 100 mW cm<sup>-2</sup>) similar to that of the E-TEK catalyst based MEAs. However, the FePc/MWCNTs based MEA showed only about 60 mW cm<sup>-2</sup> under similar conditions. MEAs with bare MWCNT cathodes were also evaluated to see whether there was any ORR activity.

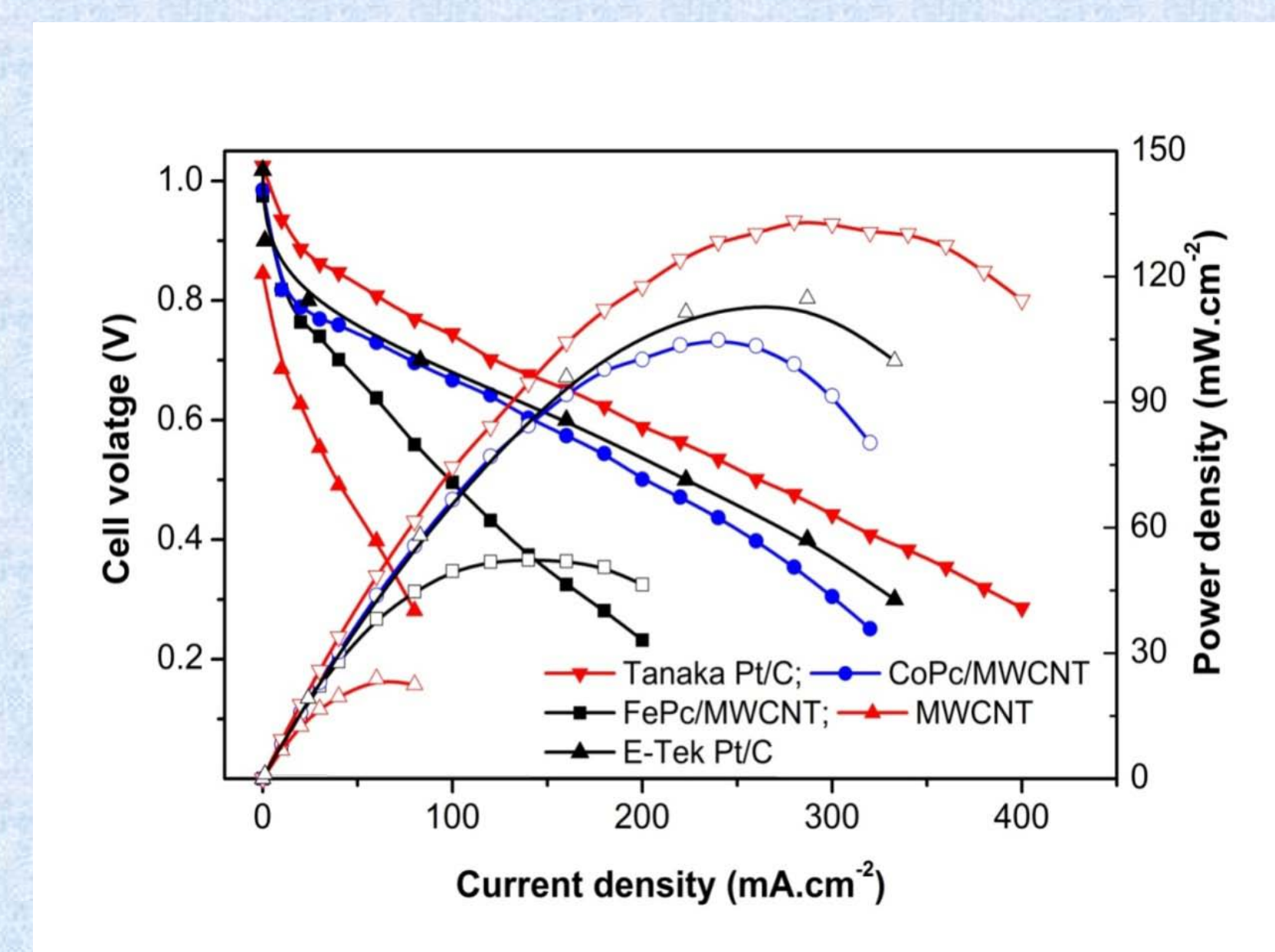


Figure 3. Fuel cell performance of MEAs with different cathode catalysts.

## Conclusions

The results obtained in this work show that MWCNT supported CoPc and FePc catalysts possess excellent electrocatalytic activity toward the ORR in alkaline media and could be used as alternative cathode catalysts in AMFCs. The fuel cell performance of the MEAs with Co phthalocyanine/MWCNT cathode was found to be almost similar to the commercial 20 wt.% Pt/C catalyst using H<sub>2</sub> and O<sub>2</sub> gases [2].

## References

- [1] I. Kruusenberg, N. Alexeyeva, K. Tammeveski, Carbon 47 (2009) 651.
- [2] I. Kruusenberg, L. Matisen, Q. Shah, A.M. Kannan, K. Tammeveski, Int. J. Hydrogen Energy 37 (2012) 4406.