

Chromium hexacyanoferrate as a cathode material in microbial fuel cells

R. Amutha · J. J. M. Josiah · J. Adriel Jebin ·
P. Jagannathan · Sheela Berchmans

Received: 7 January 2010 / Accepted: 11 July 2010 / Published online: 24 July 2010
© Springer Science+Business Media B.V. 2010

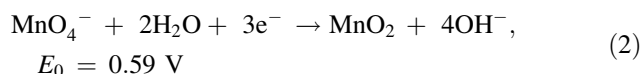
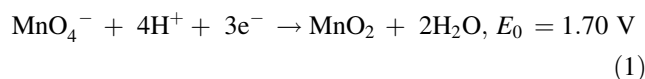
Abstract In this work, it has been demonstrated that the disadvantages associated with the use of the potassium ferricyanide solution as the catholyte in a microbial fuel cell (MFC) were overcome by using a graphite cathode electrochemically modified with chromium hexacyanoferrate (CrHCF) film. The existing use of potassium ferricyanide solution as the catholyte is limited by the need to replace the catholyte every week and it cannot be used in a sustained manner. The present work evaluates the suitability of the CrHCF modified film as a suitable cathode material in a prototype of a MFC wherein *Hansenula anomala* is used as the biocatalyst in the anode compartment. The CrHCF film was prepared in the presence of the dopant camphor sulphonic acid to improve the reversibility of the film in phosphate buffer.

Keywords Microbial fuel cells · Cathode material · Chromium hexacyanoferrate · Cyclic voltammetry · *Hansenula anomala*

1 Introduction

Microbial fuel cells (MFCs) which can convert biochemical energy to electrical energy are one of the promising sources of electrical energy generation in the future. MFCs are associated with low current and power outputs which are many orders of magnitude less than the conventional PEM fuel cells. Many technical challenges have to be overcome before the MFCs become a practical reality for renewable

energy production. Essentially, bacteria oxidize organic compounds during the metabolic process, releasing electrons, protons and carbon-di-oxide. Electrons released at the anode travel the electrical circuit and reach the cathode consisting of the electron acceptor. Protons migrate from the anode to the cathode through a proton exchange membrane which separates the anode and cathode compartment. Overall MFC performance is limited by many factors such as sluggish electron transfer associated with the microbial electron transfer, internal resistance of the MFC and the cathodic reaction. The reduction of oxygen is doubtless the best choice for the cathodic reaction not only for chemical fuel cells, but also for microbial fuel cells. However, to drive the oxygen reduction at the desired rate, a large part of the available energy is needed to establish the necessary over potential. This problem has already been recognized in the field of chemical fuel cells [1, 2]. Alternatively different cathode materials are being explored. Bergel et al. [3] found that a sea water biofilm on a stainless steel cathode increased the cathode performance in biofuel cells. Rhodes et al. [4] used biomineralised manganese oxide as a cathodic reactant. Ferric iron reduction combined with the regeneration of ferric iron by *Acidithiobacillus ferrooxidans* has also been explored as the cathodic reaction in MFCs [5, 6] Potassium permanganate solution ($E_{\text{Cat}}^0 = 1.7 \text{ V}$) has been recently used as electron acceptors in the cathode compartment by You et al. [7]. The cathodic OCP was 1.284 V, one of the highest reported for an MFC system.



R. Amutha · J. J. M. Josiah · J. Adriel Jebin · P. Jagannathan ·
S. Berchmans (✉)
Central Electrochemical Research Institute,
Karaikudi 630006, Tamilnadu, India
e-mail: sheelaberchmans@yahoo.com

Equations 1 and 2 point to a fact that in the acidic condition, permanganate actually has a much higher oxidation potential than in alkaline conditions. Therefore, an acid condition is indeed expected when using permanganate as the cathodic electron acceptor in a MFC. Based on these results, only 0.101 V was lost at the cathode. More over the permanganate cathode performance was less than that of oxygen under alkaline condition. It indicates that the performance of permanganate is limited by pH and it needs continuous replenishing of the depleted permanganate. Shantaram et al. [8] developed a fuel cell based on a sacrificial metal anode (Mg) and a cathode made of solid MnO_2 . In the anode compartment no biocatalyst was used. In the cathode compartment, the reduced Mn^{2+} was biologically regenerated by the bacteria. There are also other reports which discuss the use of MnO_2 as an alternate cathode material for MFCs. It was found that $\beta\text{-MnO}_2$ behaves better than other two types of oxides and also $\beta\text{-MnO}_2$ cathode with tubular design showed higher power density of $3773 \pm 347 \text{ mW m}^{-3}$ than cubical design using the pure culture of *K. pneumoniae* strain 117 as a biocatalyst in the anode compartment [9]. Another study reveals that MnO_2/C were chemically synthesized and used as MFC cathode containing synthetic waste water and anaerobic sewage sludge in the anode chamber [10]. The use of hexacyanoferrates as electron acceptors improves the cathode performance considerably [11–13]. However, the cathode solution has to be replenished every ten days as the solution becomes dirty brown and performance of the cell goes down. Further we observe crossover of ferricyanide to the anode compartment when the MFC is run continuously for 2–3 weeks under applied load conditions. This problem has been overcome by electrochemically coating Chromium hexacyanoferrate film on a graphite plates by a procedure developed in our lab and this method helps to deliver current from MFCs in a sustainable manner.

2 Experimental

2.1 Electrochemical preparation of Chromium hexacyanoferrate film on glassy carbon electrode

Chromium hexacyanoferrate is electrochemically grown on a glassy carbon electrode (BAS GCMF2013) by electrochemical cycling between the potential limits -0.8 to 1.1 V in a mixture of solution consisting of $0.01 \text{ M CrCl}_3 \cdot 5\text{H}_2\text{O} + 0.002 \text{ M K}_3[\text{Fe}(\text{CN})_6] + 0.08 \text{ M HCl} + 0.16 \text{ M KCl}$, vs $\text{Hg}/\text{Hg}_2\text{Cl}_2/1\text{N KCl}$ (NCE) reference electrode for 10 cycles at a scan rate of 50 mV s^{-1} . 5–10% of camphor sulphonic acid was added as a dopant during the preparation to improve the

reversibility of the film. A Pt foil was used as the counter electrode.

2.2 Electrochemical modification of the graphite cathode of the MFC Chromium hexacyanoferrate

A perforated graphite plate 6×4 cm consisting of 12 holes of $\Phi 0.4$ cm drilled at a distance of 1 cm from each other was used for electrochemical modification. The electrode was previously given a thin coating of agar for uniform adherent growth of the film. Then the electrode is subjected to electrochemical cycling between the potential limits -0.8 and 1.1 V in a solution consisting of $0.01 \text{ M CrCl}_3 + 0.002 \text{ M K}_3[\text{Fe}(\text{CN})_6] + 0.16 \text{ M KCl} + 0.08 \text{ M HCl}$ at 50 mV s^{-1} for 30 min. 5–10% of camphor sulphonic acid was added as a dopant during the preparation to improve the reversibility of the film.

2.3 Construction of the MFC

Microbial fuel cell was constructed with Perspex containing two compartments with a volume of 140 mL each. The two compartments were separated by a Nafion membrane. The cell was provided with a tight Perspex cover to maintain anaerobic conditions inside the anode chamber. The anolyte was phosphate buffer (pH 7.0) containing glucose as fuel. The yeast *Hansenula anomala* (NCIM 3341) is used as the biocatalyst in the anode compartment. A graphite felt anode of dimensions $4 \text{ cm} \times 4 \text{ cm}$ and a perforated graphite plate cathode of dimensions $6 \text{ cm} \times 4 \text{ cm}$ consisting of 12 holes of $\Phi 0.4$ cm drilled at a distance of 1 cm from each other were used in the MFC. The cathode was electrochemically modified by a film of CrHCF. The performance of the CrHCF modified electrode was investigated using three different supporting electrolytes viz. $\text{KCl} + \text{HCl}$ (pH 2.0), KCl (pH 6.) and Phosphate buffer (pH 7). Three different supporting electrolytes with three different pH conditions were chosen because the reversibility of the film and hence the electron accepting rate is different under the three conditions. To evaluate the optimum pH, the three supporting electrolytes have been evaluated.

2.4 Electrochemical characterisation

The CrHCF modified film was characterized by cyclic voltammetry and electrochemical impedance measurements using PARSTAT2263. A calomel (1.0 N KCl) electrode (NCE) and a Pt foil electrode were used as reference and a counter electrode respectively. Evaluation of the MFC was carried out by polarization measurements. The biofuel cell was discharged by applying different values of load ranging from 20 to 1000 ohms. The resulting steady state voltages

were recorded and power densities were calculated. Impedance measurements were carried out in the frequency range 100 mHz–1 MHz with an AC amplitude of 10 mV.

3 Results and discussion

3.1 Cyclic voltammetric characterization of CrHCF modified GC electrodes

Figure 1A represents the voltammogram of Chromium hexacyanoferrate modified film in HCl medium and it exhibits two sets of redox peaks. The pair of redox peaks occurring at more positive potentials ($E_{pa} = 839$ mV; $E_{pc} = 595$ mV) is irreversible in nature with a ΔE_p of 244 mV. The second set of peaks is not well defined and it occurs at 534 mV (E_{pa}) and -97 mV (E_{pc}). The peak separation is 632 mV. The ratio of the peak currents is nearly equal to one in both the sets of redox peaks. In KCl medium the pair of redox peaks appearing at more positive potentials is well defined and nearly reversible (Fig. 1B). The peaks occur at 832 mV (E_{pa}) and 781 mV (E_{pc}) respectively. The peak separation is 51 mV. The other set of redox peaks occur at 198 mV (E_{pa}) and 109 mV (E_{pc}). The anodic peak is very much smaller implying some kinetic limitations in the film during the electron transfer or due to cation transport which is required for charge balance. The ratio of currents due to anodic and cathodic peaks approaches nearly one in the case of the redox pair appearing at more positive potentials. In phosphate buffer, the two sets of redox peaks are very well defined (Fig. 1C). The first pair occurs at 166 mV (E_{pa}) and -2 mV (E_{pc}). The second pair of peaks occurs at 813 mV (E_{pa}) and 694 mV (E_{pc}) respectively. The reversibility is less compared to KCl medium. From the literature pertaining to the electrochemistry of hexacyanoferrates, it is well known that Potassium ferrocyanide/ potassium ferricyanide is a well understood standard bench mark reversible system exhibiting a single pair of redox peaks corresponding to the

ferrocyanide/ferricyanide electron transfer. However, the redox behaviour of the analogues of other metals like Cr, V, In, Ni etc., exhibit a tendency to form two pairs of redox peaks arising due to cation transport in the film [14–17]. The cation penetration is complex and it is dictated by several factors like hydrated ionic radii, channel size, chemical interactions between the ion and the film, electrostatic forces and polarizabilities. The E^0 values corresponding to the II set of redox peaks was calculated using

Table 1 Comparison of experimental and expected value of OCV

Supporting electrolyte	Expected E^0 of the cathode reaction (V)	Expected OCV (V)	Experimental OCV (V)	Loss %
HCl + KCl	0.754	1.16	0.82	30
KCl	0.806	1.218	0.52	66
Phosphate buffer	0.667	1.079	0.6	45

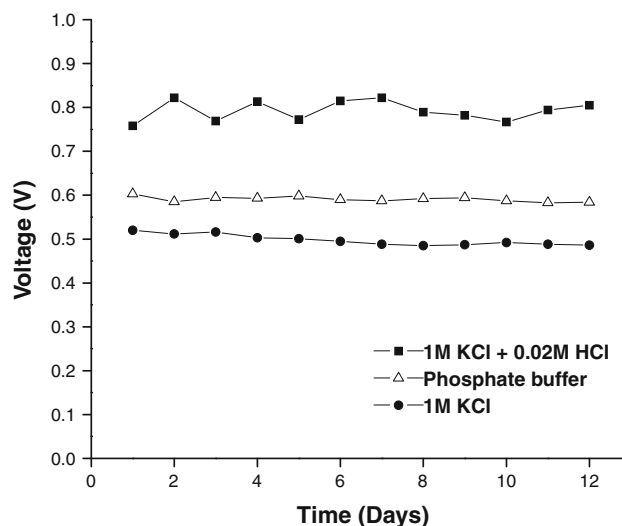


Fig. 2 Open circuit voltage variation of the MFC under three different pH conditions in the cathode compartment

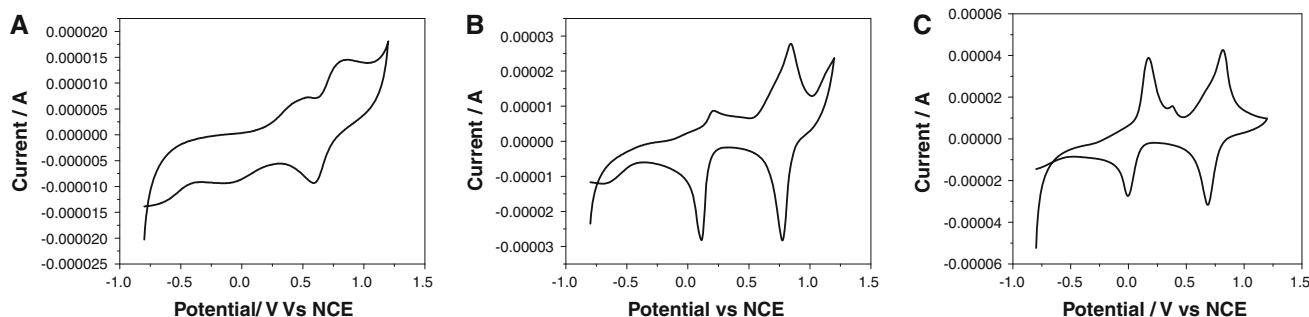


Fig. 1 A–C represent the cyclic voltammograms showing the features of CrHCF modified GC in (A) HCl + KCl (B) KCl (C) Phosphate buffer; Scan rate 50 mVs⁻¹

the formula $(E_{pa} + E_{pc})/2$. Further the reversibility of the hexacyanoferrate films are known to be better in acidic medium and KCl medium according to the literature reports. With increase in pH the reversibility is always poor. In this work the reversibility of the film in phosphate buffer has been improved in the presence of the dopant camphor sulphonic acid so that we can extend the applicability of the films to act as cathode materials in MFCs under neutral conditions also.

3.2 Open circuit voltage of the MFC

The CrHCF modified graphite cathode was incorporated in a two compartment MFC as described in the experimental section and the performance of the MFC was evaluated. The open circuit voltage obtained under three different pH conditions are depicted in Table 1 and Fig. 2. An OCV of 0.52 V was obtained in KCl medium. In acidic medium the OCV stabilized at a higher value of 0.82 V and in phosphate buffer the OCV remained stable around 0.6 V. In the presence of the film cathode the OCV is highly stable. The maximum potential generated in the anode compartment, estimated by a separate experiment was found to be -0.412 V vs NCE.

3.3 Impedance measurements

Figure 3A–C shows the impedance spectra of the cathode recorded using different supporting electrolytes. The impedance spectra were recorded with the cathode as the working electrode. At acidic pH the impedance spectrum does not show a clear semi circle. Mass transfer behavior is predominant as shown by the linear portion of the spectrum. At neutral pH, the diffusion control and activation control regions represented by a small semi circle of diameter 14 ohms, followed by a linear portion are clearly seen. In phosphate buffer also, the features are essentially the same. However the diameter of the semicircular portion representing activation control has increased to 176 ohms. In phosphate buffer activation losses are expected to be more since the R_{ct} value is higher. In acidic medium, only mass transport limits the kinetics of the cathodic reaction. Solution resistance as estimated from the impedance spectra was found to be very less (20 ohms) in KCl + HCl medium indicating that this medium is best suitable for the MFC. In the case of KCl and Phosphate buffer, the solution resistance was observed to be 130 and 100 ohms respectively. The corresponding Bode plots are shown in Fig. 3A–C. It is clearly seen that under acidic conditions the impedance

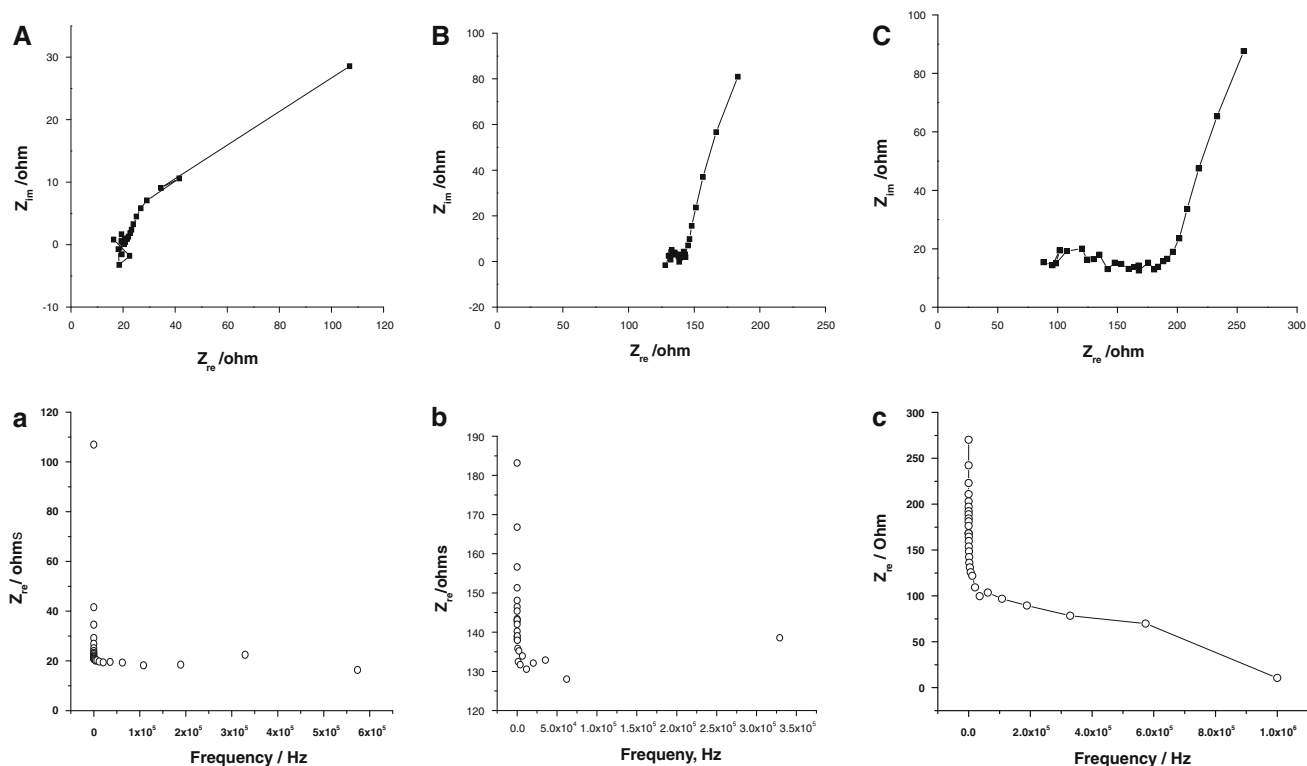


Fig. 3 A–C represent the electrochemical impedance spectra in terms of Nyquist plot for the CrHCF film in different supporting electrolytes (A) HCl + KCl (B) KCl (C) Phosphate buffer. The

corresponding Bode plots are depicted in a, b and c. Frequency range 100 mHz to 1 MHz; AC amplitude 10 mV

values remain constant at higher frequencies and in KCl medium and in phosphate buffer, the constancy is less.

3.4 Polarisation measurements

The polarization behavior of the CrHCF cathode is evaluated using the three supporting electrolytes KCl + HCl, KCl, phosphate buffer and are presented in Fig. 4A–C. From the polarization behaviour of the MFC, it can be observed that a power density of 6.67 W m^{-3} was obtained under acidic condition which is nearly 17 times higher compared to the power density obtained under neutral conditions. A maximum power density of 0.45 W m^{-3} was obtained in KCl medium and a maximum power density of 0.41 W m^{-3} was obtained in phosphate buffer. Under acidic conditions there is no limitation imposed by rate of protons arriving at the cathode through the membrane separating the anode and cathode compartment. The results

pertaining to the use of ferricyanide as electron acceptor using the same biocatalyst *Hansenula anomala* with the same MFC configuration have been reported by us earlier and we have reported maximum power density of 2.34 W m^{-3} in our earlier work which is lower by 2.8 times compared to the CrHCF films in KCl + HCl medium [18].

It has been suggested in the literature that the hexacyanoferrates can reduce oxygen. The O_2 molecules enter the ferrocyanide vacancies and they are in a position to accept electrons from Fe (II) atoms [17]. Figure 5A and B demonstrate that the CrHCF films can electrocatalytically reduce oxygen under acidic as well as neutral conditions. In acidic condition, it is seen that the redox characteristics of the film is maintained even after subjected to oxygen reduction. This demonstrates that the film is stable and can be used for greater lengths of time. However, in phosphate buffer, the redox characteristics of the film are lost after oxygen reduction cycle. This also points towards the less

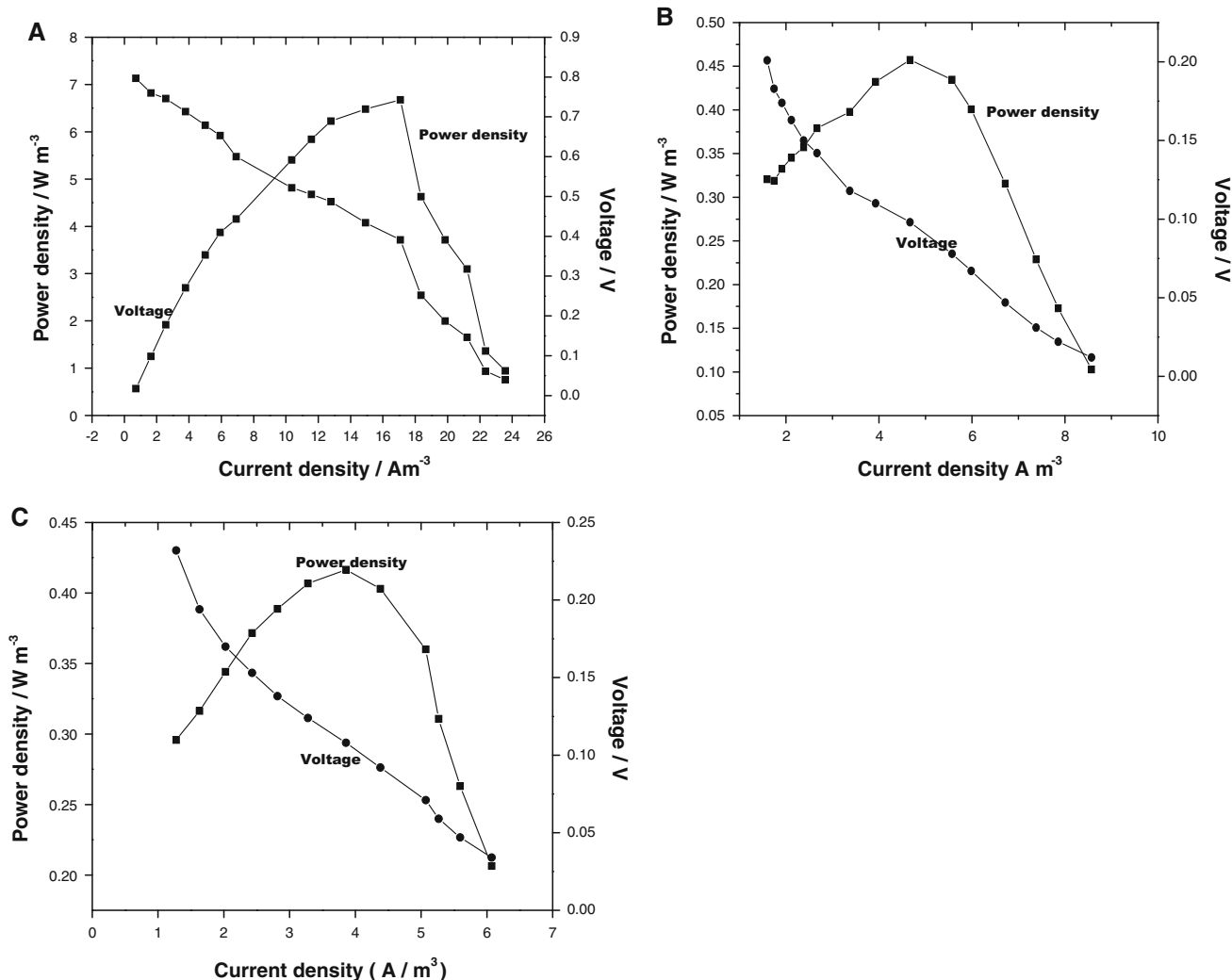


Fig. 4 Polarization curve for the MFC in three different supporting electrolytes (A) KCl + HCl (B) KCl (C) Phosphate buffer

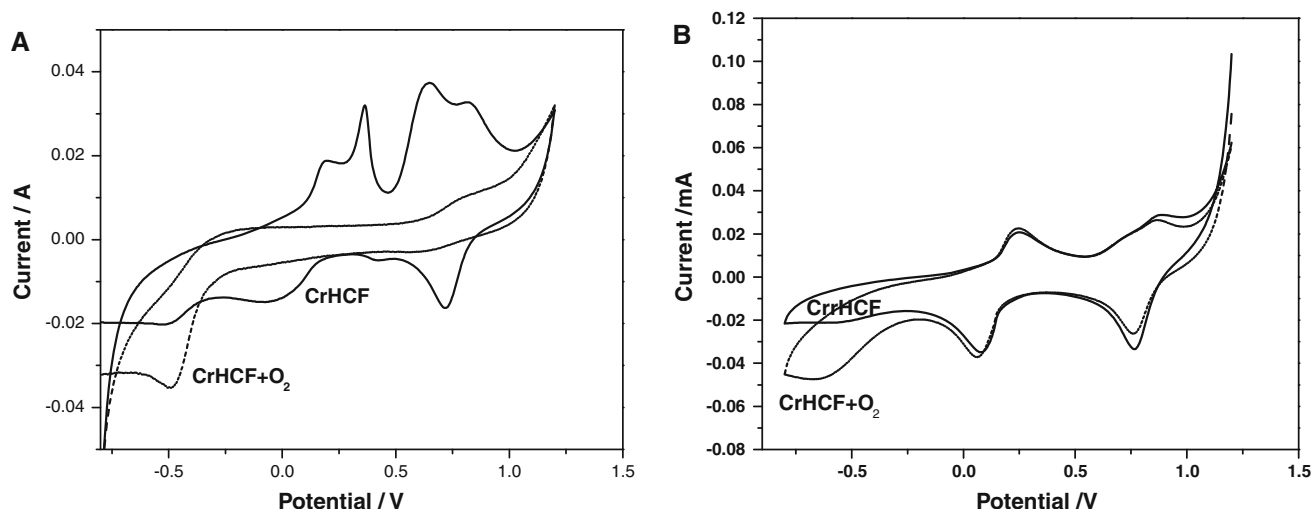


Fig. 5 Cyclic voltammogram of CrHCF films in (A) Phosphate buffer (B) KCl + HCl; Scan rate 50 mVs^{-1}

suitability of the films under neutral conditions in MFCs. Hence under acidic conditions, CrHCF films accept electrons from the anode compartment which is transferred to oxygen and the film gets oxidized back and hence there will be no depletion of the electron acceptors occurring in the cathode compartment and the currents are derived in a sustainable manner.

4 Conclusions

In this work it has been demonstrated that how the CrHCF film cathode can generate current in a sustained manner. The OCV of the MFC remains highly stable. The replacement of catholyte is completely avoided in the present configuration Power density as high as 6.67 W m^{-3} is derived from the biofuel cells operating under acidic conditions in the cathode compartment. Oxygen reduction coupled with CrHCF reoxidation avoids depletion of the electron acceptors thereby improving the sustainability of the MFC.

Acknowledgment The authors wish to acknowledge Ministry of New and Renewable Energy, New Delhi, India for funding this work.

References

1. Zhao F, Harnisch F, Schroder U, Scholz F, Bogdanoff P, Herrmann I (2006) *Environ Sci Technol* 40:5193–5199

2. Oh S, Min B, Logan BE (2004) *Environ Sci Technol* 38:4900–4904
3. Bergel A, Feron D, Mollica A (2005) *Electrochem Commun* 7:900–904
4. Rhoads A, Beyenal H, Lewendowski Z (2005) *Environ Sci Technol* 39:4666–4671
5. Heijne AT, Hamelers HVM, De wilde V, Rozendal RA, Buisman CJN (2006) *Environ Sci Technol* 40:5200–5205
6. Prasad D, Sivaam TK, Berchmans S, Yegnaraman V (2006) *J Power Sources* 160:991–996
7. You S, Zhao Q, Zhang J, Jiang J, Zhao S (2006) *J Power Sources* 162:1409–1415
8. Shantaram A, Beyenal H, Raajam R, Veluchamy A, Lewendowski Z (2005) *Environ Sci Technol* 39:5037–5042
9. Zhang L, Liu C, Zhuang L, Li W, Zhou S, Zhang J (2009) *Biosens Bioelectron* 24:2825–2829
10. Roche I, Katuri K, Scott K (2010) *J Appl Electrochem* 40:13–21
11. Rabaey K, Verstraete W (2005) *Trends Biotechnol* 23:291–298
12. Oh S, Min B, Logan BE (2004) *Environ Sci Technol* 38:4900–4904
13. Rabaey K, Lissens G, Siciliano SD, Verstraete W (2003) *Biotechnol Lett* 25:1531–1535
14. Jiang M, Zhou X, Zhao Z (1990) *J Electroanal Chem* 287:389–394
15. Kuleza PJ, Faszynska M (1988) *J Electroanal Chem* 252:461–466
16. Shaojun D, Fengbin L (1986) *J Electroanal Chem* 210:31–44
17. Itaya K, Uchida I (1986) *Acc Chem Res* 19:162–168
18. Prasad D, Arun S, Murugesan M, Padmanaban S, Satyanarayanan RS, Berchmans S, Yegnaraman V (2007) *Biosens Bioelectron* 22:2604–2610