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ORIGINAL PAPER

# Improved performance of the direct methanol redox fuel cell

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**Abstract** Advancements in the performance of the direct methanol redox fuel cell (DMRFC) were made through anolyte/catholyte composition and cell temperature studies. Catholytes prepared with different iron salts were considered for use in the DMRFC in order to improve the catholyte charge density (i.e., iron salt solubility) and fuel cell performance. Following an initial screening of different iron salts, catholytes prepared with $FeNH_4(SO_4)_2$, $Fe(ClO_4)_3$ or $Fe(NO_3)_3$ were selected and evaluated using electrolyte conductivity measurements, cyclic voltammetry and fuel cell testing. Solubility limits at 25 °C were observed to be much higher for the $Fe(ClO_4)_3$ (>2.5 M) and $Fe(NO_3)_3$ (>3 M) salts than $FeNH_4(SO_4)_2$ ($\sim$1 M). The $Fe(ClO_4)_3$ catholyte was identified as a suitable candidate due to its high electrochemical activity, electrochemical reversibility, observed half-cell potential (0.83 V vs. SHE at 90 °C) and solubility. DMRFC testing at 90 °C demonstrated a substantial improvement in the non-optimized power density for the perchlorate system (79 mW cm$^{-2}$) relative to that obtained for the sulfate system (25 mW cm$^{-2}$). Separate fuel cell tests showed that increasing the cell temperature to 90 °C and increasing the methanol concentration in the anolyte to 16.7 M (i.e., equimolar $H_2O/CH_3OH$) yield significant DMRFC performance improvements. Stable DMRFC performance was demonstrated in short-term durability tests.

**Keywords** Redox couple · Methanol · Fuel cell · Ferric · Ferrous

## 1 Introduction

In an era of ever increasing demand for portable power, promising technologies such as direct methanol fuel cells (DMFCs) are being investigated by a large number of researchers across the globe [1–3]. The DMFC is targeted towards micro and portable applications due to the facile storage/transportation of the fuel and high volumetric energy/charge density of the fuel (4.62 kWh L$^{-1}$/3.95 kAh L$^{-1}$ at 25 °C). These specific markets are generally not considered for the $H_2$ proton exchange membrane fuel cell (PEMFC) due to the low volumetric energy/charge density of the fuel [approx. 0.9 kWh L$^{-1}$/0.7 kAh L$^{-1}$ at 34.5 MPa (5000 psi) and 25 °C]. Other DMFC advantages over the PEMFC include no need for auxiliary humidification or cooling equipment [4, 5].

There are a number of limitations to the DMFC, however, such as cathode flooding, fuel cross-over, $CO_2$ product removal at the anode, and sluggish anode and cathode kinetics. Water dragged from the anode to the air cathode by the electro-osmotic effect and water produced by the cathode reaction significantly impact the degree of cathode flooding [6]. Currently, Nafion® is the most widely used membrane in DMFC systems due to its good proton conductivity, mechanical durability and chemical resistance. However, liquid fuels are known to permeate through Nafion® at rates

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where fuel loss and cathode depolarization become an issue, ultimately leading to reduced cell performance [7, 8]. Consequently, it is common to use low fuel concentrations relative to the reaction stoichiometry concentration to reduce fuel crossover in conventional DMFCs. For example, methanol concentrations in the range of 0.75–2 M are typically used [7, 9, 10] which are significantly lower than the reaction stoichiometry concentration of approximately 17 M $CH_3OH$. In conventional DMFCs, fuel crossover can cause cathode depolarization through two related but fundamentally different phenomena: (1) fuel oxidation at the cathode (Pt catalyst), creating a mixed potential, and (2) decreasing surface concentration of oxygen at the cathode due to the consumption of oxygen via direct fuel oxidation, leading to a Nernstian voltage loss and increased kinetic overpotential. A number of approaches have been investigated by various research groups to address methanol crossover, which include developing new membranes [11], modifying membranes [12], introducing fuel additives [13], optimizing operating conditions [14], designing novel electrodes [15] and employing methanol-tolerant cathode catalysts [16–18].

Our work involves an alternative approach to the classical DMFC architecture in which the air cathode containing Pt is substituted by a metal-ion redox couple (e.g., $Fe^{2+}/Fe^{3+}$) over a carbon cathode containing no platinum group metal (PGM) catalyst. This system is referred to herein as the direct methanol redox fuel cell (DMRFC). Initial pioneering work on this type of hybrid system was conducted by Fatih et al., but with a hydrogen redox fuel cell [19, 20]. The relevant electrochemical equations for the DMRFC using methanol fuel at the anode and the $Fe^{2+}/Fe^{3+}$ redox couple at the cathode are given below:

$$CO_2 + 6H^+ + 6e^- \leftarrow CH_3OH + H_2O \quad \text{Anode} \quad E^0_{half} = 0.06\ \text{V vs. SHE} \quad (1)$$

$$6Fe^{3+} + 6e^- \rightarrow 6Fe^{2+} \quad \text{Cathode} \quad E^0_{half} = 0.77\ \text{V vs. SHE} \quad (2)$$

$$CH_3OH + H_2O + 6Fe^{3+} \rightarrow CO_2 + 6H^+ + 6Fe^{2+} \quad \text{Overall} \quad E^0 = 0.71\ \text{V} \quad (3)$$

The DMRFC offers some significant advantages over the conventional DMFC including no PGM catalyst at the cathode, the ability to utilize high fuel concentrations at the anode (e.g., equimolar $CH_3OH/H_2O$, approximately 17 M $CH_3OH$) without introducing significant issues at the selective cathode, no cathode flooding as it is an all-liquid system and enhanced design flexibility with respect to the cathode (i.e., no triple phase boundary constraints, use of 3-D electrode, etc.). However, there are some challenges associated with the DMRFC which include regeneration of the redox couple, membrane contamination by the redox couple, crossover of the redox couple and mismatched charge density of the anolyte and catholyte. After the redox couple oxidant is reduced during cell discharge, it must be regenerated externally by chemical, electrochemical [21] or biological means [22], which will affect the system's overall efficiency and simplicity.

The volumetric charge density of the anolyte and catholyte governs the volume of the electrolyte reservoirs required for a desired energy output. In our previous work on the DMRFC [23, 24], $FeNH_4(SO_4)_2$ and $FeSO_4$ salts were used to prepare the catholyte, in which case the aqueous solubility limit of the iron salt is less than 1 M at 25 °C. As each methanol molecule carries six times the number of electrons as a ferric ion, there is an issue of mismatched anolyte/catholyte charge densities, particularly at high methanol concentrations.

A primary objective of this work was to increase the DMRFC catholyte charge density and improve the performance of the DMRFC by investigating catholytes prepared with irons salts apart from $FeNH_4(SO_4)_2$. Membrane compatibility, electrolyte conductivity, cyclic voltammetry and fuel cell tests were used to evaluate and screen the selected iron salts. Additional studies were performed to investigate the effect of the anolyte methanol concentration and the cell temperature on the DMRFC performance. A series of short DMRFC durability tests are also included.

## 2 Experimental

All electrolytes were prepared with deionized water (18 MΩ cm) in glassware cleaned with equal parts of concentrated $HNO_3$ (ACS, Fisher Scientific) and concentrated $H_2SO_4$ (ACS, Fisher Scientific). Electrolytes containing the $Fe^{2+}/Fe^{3+}$ redox couple were based on one of three anions: $ClO_4^-$, $NO_3^-$ or $SO_4^{2-}$. Iron perchlorate electrolytes were prepared with $Fe(ClO_4)_3{\cdot}6H_2O$ (non-yellow, GFS Chemicals), no acid; iron nitrate electrolytes were prepared with $Fe(NO_3)_3{\cdot}9H_2O$ (ACS, Fisher Scientific), no acid; iron sulfate electrolytes were prepared with $FeNH_4(SO_4)_2{\cdot}12H_2O$ (ACS, Fisher), $FeSO_4{\cdot}12H_2O$ (ACS, Fisher) and $H_2SO_4$ (ACS, Fisher Scientific). No acid was added to the iron perchlorate or iron nitrate solutions as these salts already contain a sufficient amount of residual perchloric or nitric acid, respectively, to produce a strongly acidic solution. For instance, the pH of the 2.5 M $Fe(ClO_4)_3$ and 1 M $Fe(NO_3)_3$ electrolytes were approximately −0.25 and 0.5, respectively. An Oaklon 110 series pH meter was used for the pH measurements. All Nafion® 112 membranes used in the various experiments were cleaned and protonated by soaking in deionized $H_2O$ for 2 h, boiling in 3% $H_2O_2$ for 30 min, rinsing in deionized $H_2O$, boiling in 0.5 M $H_2SO_4$ for 30 min, rinsing in deionized $H_2O$ and finally storing in deionized $H_2O$ for at least 24 h.

Chemical compatibility of the sulfate, perchlorate and nitrate electrolytes with the Nafion® 112 membrane was determined by measuring any difference in dry weight of the membrane before and after exposure to the electrolytes. Nafion® membranes were initially dried in vacuum at 60 °C overnight, weighed and then hydrated. The hydrated membranes were then immersed in a saturated or nearly saturated solution of ferric perchlorate (~3 M), ferric nitrate (~3.9 M) or ferric ammonium sulfate (~1 M) at 90 °C and left overnight. The membranes were finally rinsed with deionized water, soaked in deionized water, dried by the method above and weighed.

The ionic conductivity of various redox electrolytes was measured with a YSI 3200 conductivity meter. Electrolytes were kept in a sealed glass cell to avoid evaporation and were immersed in a constant temperature bath (Neslab EX-7, Thermo Electron) to achieve the desired temperature. Conductivity measurements were taken once the electrolyte reached the desired temperature.

Cyclic voltammetry experiments were conducted at 90 °C using either a 5 mm diameter glassy carbon (GC) (AFE1E050GC, Pine Instruments) or 5 mm diameter Pt (EDI101, Radiometer) working electrode. The counter electrode was a Pt flag (XM120, Radiometer) and the reference electrode was an Ag/AgCl reference electrode (XR300, Radiometer). The temperature of the glass cell was maintained at 90 °C by submerging the cell in a constant temperature bath (Neslab EX-7, Thermo Electron) and electrolytes were de-aerated by bubbling $N_2$ for 30 min at room temperature prior to testing under static conditions. The GC electrode was prepared by rinsing with alcohol, polishing with 0.05 µm alumina, rinsing with deionized water, sonicating in deionized water for 2 min and finally rinsing in deionized water. The Pt electrode was prepared by rinsing with alcohol, submerging in a hot solution of 1:1 concentrated sulfuric acid (ACS, Fisher) and 30% w/w hydrogen peroxide (ACS, Fisher) for 5 min followed by rinsing with deionized water. A Solartron 1260 frequency response analyzer (FRA) was used to obtain the internal cell resistance for IR correction of the cyclic voltammograms. Stable voltammograms were acquired after 10 cycles.

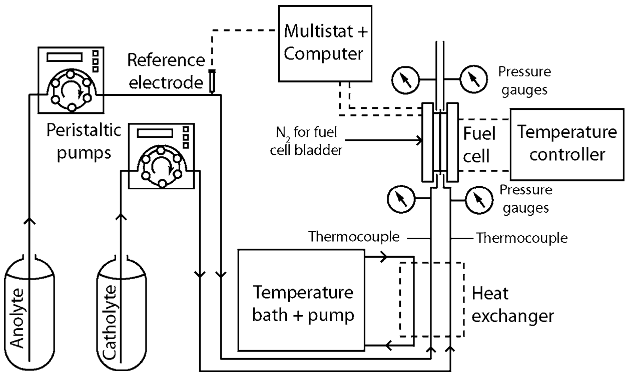

**Fig. 1** Schematic of the direct liquid redox fuel cell test system

DMRFC performance testing was performed in the single-pass fuel cell test system shown in Fig. 1. The anode catalyst loading for all fuel cell testing was 2 mg $cm^{-2}$ (40% 1:1 a/o Pt/Ru on Vulcan XC-72, E-Tek) on TGP-H-060 carbon fiber paper (CFP). Nafion® ionomer (5% in $H_2O$/alcohol, Aldrich) was added to the catalyst ink as a binding agent in the amount of 30% w/w. Anolytes for fuel cell testing were prepared with methanol (electronic grade, Fisher) and either $HClO_4$ or $H_2SO_4$, depending on whether the catholyte contained perchlorate or sulfate anions, respectively. A serpentine flow field with a channel width and depth of 0.84 and 0.46 mm, respectively, was used at the anode. The cathode consisted of three layers of 370 µm thick TGP-H-120 CFP with no PGM catalyst packed into an empty 1 mm deep pocket. The cathode was supplied with a $Fe^{2+}/Fe^{3+}$ redox electrolyte incorporating either $SO_4^{2-}$ or $ClO_4^-$ anions. A Nafion® 112 membrane was employed for all DMRFC tests. Nafion® membranes were not hot-pressed to the electrodes. In all configurations, the nitrogen bladder (see Fig. 2 in our previous work [23]) was

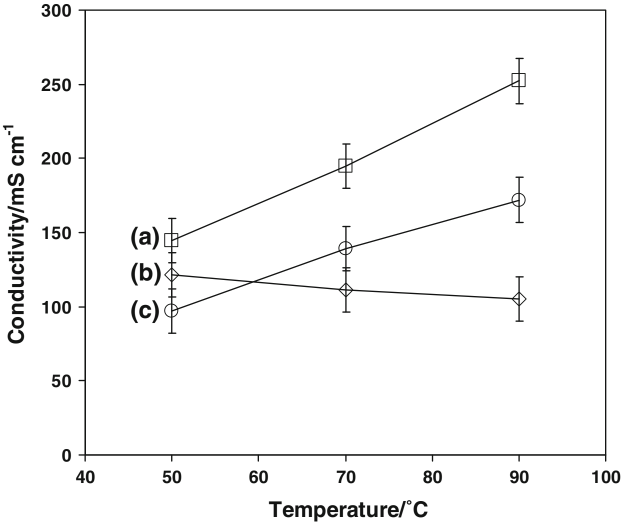

**Fig. 2** Electrolyte conductivities as a function of temperature for (*a*) 2.5 M $Fe(ClO_4)_3$; (*b*) 1 M $FeNH_4(SO_4)_2$/0.5 M $H_2SO_4$; (*c*) 3 M $Fe(NO_3)_3$

pressurized to 30 psig in order to compress the fuel cell. The cell impedance used for IR-correction of polarization curves was obtained by taking the real component of the cell impedance measured at 20 kHz using a GwINSTEK LCR-821 unit. All fuel cell testing was performed after at least 30 min of potentiostatic cell conditioning at 0 V.

## 3 Results and discussion

In determining which non-sulfate iron salts would be suitable candidates for the DMRFC catholyte, the cost, chemical compatibility, half-cell potential, catalyst poisoning effects, purity, availability and solubility (when known) were considered. Iron salts with acetate, acetylacetonate, ammonium citrate, carbonate, chloride, citrate, hypophosphite, nitrate, oxalate, perchlorate, phosphate or tetrafluoroborate anions were initially screened. A list of all iron salts considered including reasons for excluding various salts is shown in Table 1. For some anions, such as citrate and oxalate, ligand effects contributed to the decision to exclude these salts from the study as they negatively shift the half cell potential of the $Fe^{2+}/Fe^{3+}$ redox couple. Upon completing the initial screening process, it was determined that nitrate and perchlorate iron salts should be further investigated through electrolyte conductivity, cyclic voltammetry and fuel cell tests.

The aqueous solubility of $Fe(ClO_4)_3{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ at 25 °C was experimentally determined to be greater than 2.5 and 3 M, respectively, which compares favourably with the aqueous solubility of $FeNH_4(SO_4)_2$ ($\sim$1 M) [27]. The $Fe(NO_3)_3{\cdot}9H_2O$ salt melts at 47 °C and thus preparation of a saturated ferric nitrate solution simply involves heating the salt. Positive results were obtained from the chemical compatibility test for Nafion® 112 membranes in saturated or nearly saturated solutions of ferric perchlorate and ferric nitrate at 90 °C. No significant change in the dry membrane weight was observed after overnight exposure to the electrolytes indicating no rapid membrane degradation due to oxidation. It should also be noted that previous differential scanning calorimetry tests [23] showed chemical compatibility of methanol and the $Fe^{2+}/Fe^{3+}$ redox couple up to 200 °C in the presence and absence of carbon, which confirms the selectivity of the $Fe^{2+}/Fe^{3+}$ redox cathode.

The electrolyte conductivity of 2.5 M $Fe(ClO_4)_3$, 3 M $Fe(NO_3)_3$ and 1 M $FeNH_4(SO_4)_2$/0.5 M $H_2SO_4$ was measured at 50, 70 and 90 °C. High concentrations for each type of iron salt were selected to determine the conductivity for fuel cell conditions. The conductivity measurements, shown in Fig. 2, indicate that the non-sulfate electrolytes exhibited higher conductivity than the sulfate containing electrolyte, particularly at higher temperatures. It is interesting to note that the conductivity of the sulfate containing electrolyte decreases with temperature whereas the conductivity of the other electrolytes increases. This trend can be attributed to the formation of complexes such as $FeH(SO_4)_2$ and $HSO_4^-$ at elevated temperatures [28]. Based on the conductivity data acquired here, it is apparent that the conductivities of the ferric nitrate and ferric perchlorate electrolytes are sufficiently high for employment in the DMRFC given the good performance obtained with ferric sulfate which has a lower conductivity.

Cyclic voltammetry experiments were conducted at 90 °C to quantify the electrochemical activity and reversibility over Pt and GC of electrolytes prepared with the three iron salts: (a) 1 M $Fe(ClO_4)_3$, (b) 1 M $FeNH_4(SO_4)_2$/0.5 M $H_2SO_4$ and (c) 0.05 M and 1 M $Fe(NO_3)_3$. The electrochemical activity over Pt provides a meaningful baseline for comparison of the activity over GC, which is

**Table 1** List of ferric salts considered for use in the DMRFC catholyte

| Ferric salt anion | Molecular formula | Half cell potential/ V vs. SHE | Ref. | Primary reasons for exclusion |
|---|---|---|---|---|
| Acetylacetonate | $C_5H_7O_2^-$ | – | – | Very expensive |
| Acetate | $CO_2CH_3^-$ | – | – | Unavailable |
| Ammonium citrate | $NH_4C_6H_8O_7^{2-}$ | 0.03 | [25] | Low $E^0$, unknown purity |
| Carbonate | $CO_3^{2-}$ | – | – | Unavailable |
| Chloride | $Cl^-$ | 0.7 | [26] | Pt catalyst poison |
| Citrate | $H_2C_6H_5O_7^-$ | 0.03 | [25] | Low $E^0$, low purity |
| Hypophosphite | $H_2PO_2^-$ | – | – | Very expensive, unknown purity |
| Nitrate | $NO_3^-$ | – | – | – |
| Oxalate | $C_2O_4^{2-}$ | 0.05 | [25] | Low $E^0$, very expensive |
| Perchlorate | $ClO_4^-$ | – | – | – |
| Phosphate | $PO_4^{3-}$ | 0.44 | [26] | Low $E^0$ |
| Sulfate | $SO_4^{2-}$ | – | – | – |
| Tetrafluoroborate | $BF_4^-$ | – | – | Very expensive |

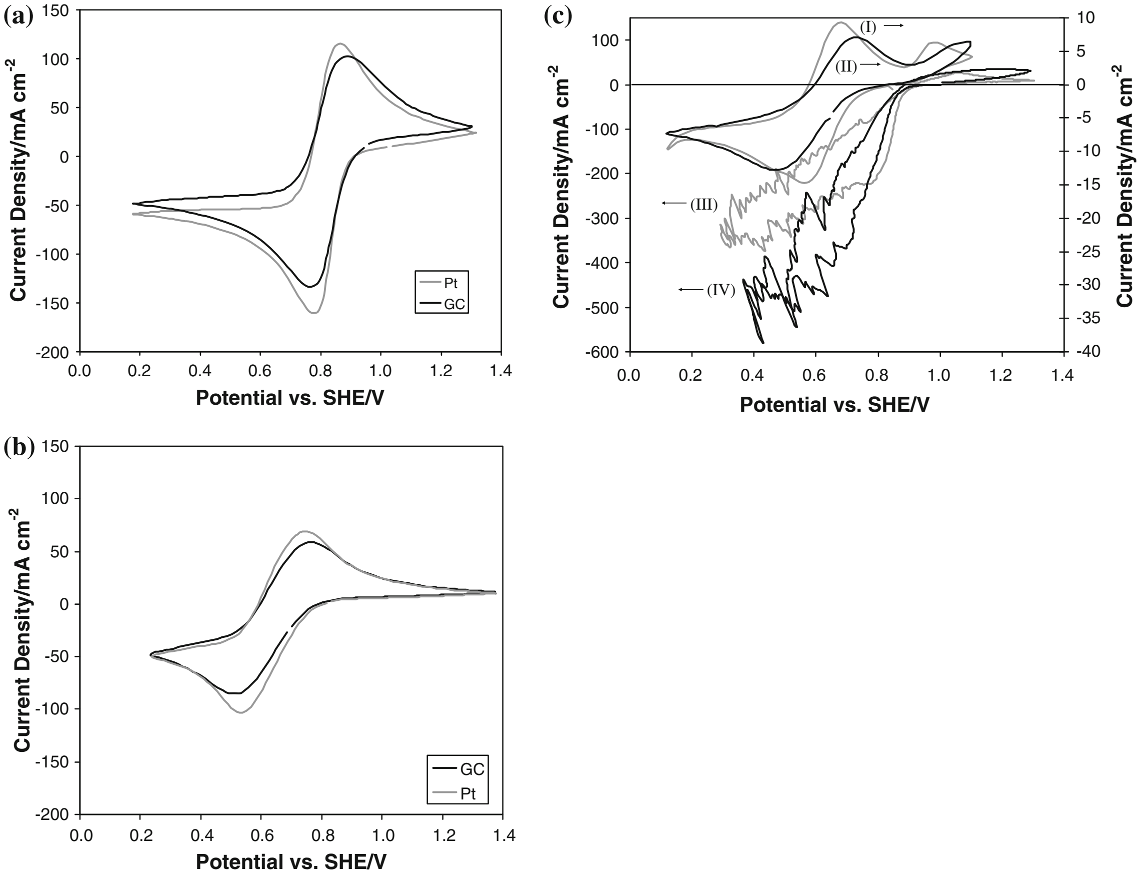

**Fig. 3** Cyclic voltammograms (90 °C, 50 mV $s^{-1}$ scan rate, IR-corrected) over Pt and GC working electrodes for electrolytes comprised of **a** 1 M $Fe(ClO_4)_3$, **b** 1 M $FeNH_4(SO_4)_2$/0.5 M $H_2SO_4$, and **c** (I) Pt, 0.05 M $Fe(NO_3)_3$, (II) GC, 0.05 M $Fe(NO_3)_3$, (III) Pt, 1 M $Fe(NO_3)_3$, and (IV) GC, 1 M $Fe(NO_3)_3$

chemically similar to the carbon fiber paper (CFP) used in the DMRFC cathode. The voltammograms for the iron electrolytes, shown in Fig. 3, indicate comparable electrochemical activity between Pt and GC for the perchlorate (Fig. 3a) and sulfate (Fig. 3b) electrolytes. For the nitrate electrolyte (Fig. 3c), the electrochemical response was largely dependent on the concentration of the iron salt.

Initially, the 1 M $Fe(NO_3)_3$ electrolyte was tested and irreversible electrochemical behaviour with a significant degree of noise was observed. Consequently, a lower concentration was tested and it was observed that at 0.05 M $Fe(NO_3)_3$, voltammograms with little noise and reversible behaviour could be generated on Pt and GC. The irreversible electrochemical response of 1 M $Fe(NO_3)_3$ is likely related to the instability of $NO_3^-$ ions. Trace impurities of metal ions such as $Ag^+$, $Cu^{2+}$ and $Sn^{2+}$ are known to catalyze the reduction of $NO_3^-$ by $Fe^{2+}$ [29], which can lead to a variety of reaction products such as $NO_2^-$, $N_2O$ and NO [26]. At a $Fe(NO_3)_3$ concentration of 1 M, it may be the case that the Pt/GC electrode is being poisoned by products of $NO_3^-$ reduction. This issue is not fully understood and requires further investigation. One of the primary objectives of this work was to improve the charge density of the redox electrolyte; however, a reversible electrochemical response could not be generated at a concentration of 1 M $Fe(NO_3)_3$.

The anodic and cathodic peak current densities ($i_p$), peak potentials ($E_p$) and apparent half cell potential ($E$) for the perchlorate, nitrate and sulfate voltammograms from Fig. 3 are shown in Table 2. The data for the 0.05 M $Fe(NO_3)_3$ system was included in Table 2 for completeness but since this electrolyte is not acceptable for use as a catholyte in a DMRFC, no further discussion on the nitrate voltammogram will be given. From Table 2, it is apparent that the peak current density over GC is reduced by roughly 15 and 20% relative to that over Pt for the perchlorate and sulfate electrolytes, respectively. The peak current density for the perchlorate system over GC is more than 50% greater than that observed for the sulfate system. In addition, the electrochemical reversibility of the perchlorate system, represented by the difference in peak potentials, is superior to that of the sulfate system over both Pt and GC. The advantages of the perchlorate system with respect to the electrochemical activity and reversibility indicate that this

**Table 2** Summary of anodic and cathodic peak current densities ($i_p$), peak potentials ($E_p$) and apparent half-cell potentials ($E$) for cyclic voltammograms shown in Fig. 3

| Electrolyte | Electrode | $i_{p,a}$/mA cm$^{-2}$ | $i_{p,c}$/mA cm$^{-2}$ | $E_{p,a}$/V vs. SHE | $E_{p,c}$/V vs. SHE | $E_{p,a} - E_{p,c}$/V | $E$/V vs. SHE |
|---|---|---|---|---|---|---|---|
| 1 M $Fe(ClO_4)_3$ | Pt | 159 | 166 | 0.86 | 0.78 | 0.08 | 0.82 |
| 1 M $Fe(ClO_4)_3$ | GC | 137 | 143 | 0.89 | 0.77 | 0.12 | 0.83 |
| 1 M $FeNH_4(SO_4)_2$, 0.5 M $H_2SO_4$ | Pt | 93 | 107 | 0.75 | 0.54 | 0.21 | 0.65 |
| 1 M $FeNH_4(SO_4)_2$, 0.5 M $H_2SO_4$ | GC | 75 | 87 | 0.77 | 0.51 | 0.26 | 0.64 |
| 0.05 M $Fe(NO_3)_3$ | Pt | 12 | 13 | 0.67 | 0.56 | 0.11 | 0.62 |
| 0.05 M $Fe(NO_3)_3$ | GC | 9 | 10 | 0.72 | 0.47 | 0.25 | 0.60 |

system is a better candidate for use as a DMRFC catholyte than the sulfate system. The apparent $Fe^{2+}/Fe^{3+}$ half-cell potential, taken as the midpoint of the peak potentials, is significantly higher for the perchlorate electrolyte (0.83 V vs. SHE) than that observed for the sulfate electrolyte (0.64 V vs. SHE). The difference is due to ligand effects of the sulfate and perchlorate anions on the $Fe^{2+}$ and $Fe^{3+}$ cations. In general, all ligands have a certain tendency to form complexes with a particular metal ion, which is expressed by the formation constant of the complex. In the case of a redox couple, if the ligand has a stronger preference to form complexes with one metal ion over the other, the half-cell potential can shift due to changes in the relative activity of the metal ions. The $Fe^{2+}/Fe^{3+}/C_3H_5O(COO)_3^{3-}$ (citrate) system demonstrates this phenomenon quite well. The formation constant for the $Fe(II)(cit)^-$ complex is 3.08 while the formation constant for the Fe(III)(cit) complex is 12.5 [27]. Consequently, a larger fraction of the $Fe^{3+}$ ions are complexed than $Fe^{2+}$ ions and the $Fe^{3+}/Fe^{2+}$ activity ratio is reduced. This has a direct Nernstian impact on the half-cell potential of the redox couple, which explains the negative shift in the standard half-cell potential of the $Fe^{2+}/Fe^{3+}$ redox couple from 0.77 V versus SHE [26] to 0.03 V versus SHE after complexation with citrate [25]. Overall, the perchlorate electrolyte is a strong candidate as a DMRFC catholyte because it exhibits significantly greater electrochemical activity, electrochemical reversibility, half-cell potential and solubility relative to the sulfate electrolyte.

DMRFC testing was performed to identify operating conditions that yield improved fuel cell performance and to observe the short-term performance stability of the DMRFC. The DMRFC tests can be divided into four groups which investigate

(1) The effect of the anion in the iron salt (incorporates the iron concentration effect)
(2) The effect of the methanol concentration in the anolyte
(3) The effect of the cell temperature
(4) The short-term durability of the DMRFC

DMRFC tests observing the effect of the anion in the iron salt were performed at 90 °C using catholytes prepared with either 2.5 M $Fe(ClO_4)_3$ or 1 M $FeNH_4(SO_4)_2$/0.5 M $H_2SO_4$ (a DMRFC test using a 1 M $Fe(NO_3)_3$ catholyte produced no significant amount of power and had extremely poor stability). The iron concentration in the catholyte for both cases was in the vicinity of the solubility limit for that particular salt. The anolyte consisted of 1 M $CH_3OH$ and either 0.2 M $HClO_4$ or 0.1 M $H_2SO_4$, depending on the iron salt being used in the catholyte. The anolyte included some acid in order to establish ionic conductivity between the anode and the Ag/AgCl reference electrode, shown in Fig. 1. The cell and individual electrode polarization behaviour for DMRFC tests observing anion effects are shown in Fig. 4. The results indicate that the perchlorate system exhibits a significantly higher open-circuit potential (OCP), lower ohmic losses and superior non-optimized power density (79 mW cm$^{-2}$) relative to the sulfate system (25 mW cm$^{-2}$).

The individual anode and cathode polarizations shown in Fig. 4 allow for a deeper understanding of the influence of the anion. The cathode polarization behaviour indicates a >200 mV positive shift in the cathode OCP when switching from a sulfate system to a perchlorate system. The primary reason for this shift in half cell potential is the difference in the interaction of the iron ions with the sulfate and perchlorate ligands. If a ligand preferentially binds to one redox couple ion over the other, the activity of that preferred ion will be reduced and will affect the potential of the redox couple in a Nernstian fashion. Since perchlorate anions are known to exhibit weak ligand effects [30], it is likely that the oxidizing ability of the ferric ion is greater in the perchlorate system. More detailed analyses would be required to confirm this. The anode polarizations show higher overpotential for the perchlorate system. Two factors in the perchlorate system that may be responsible include: (1) perchlorate anions influencing the polarization behaviour of methanol oxidation, and (2) increased anode depolarization due to the higher crossover rate of ferric ions from the cathode to the anode. The latter phenomenon

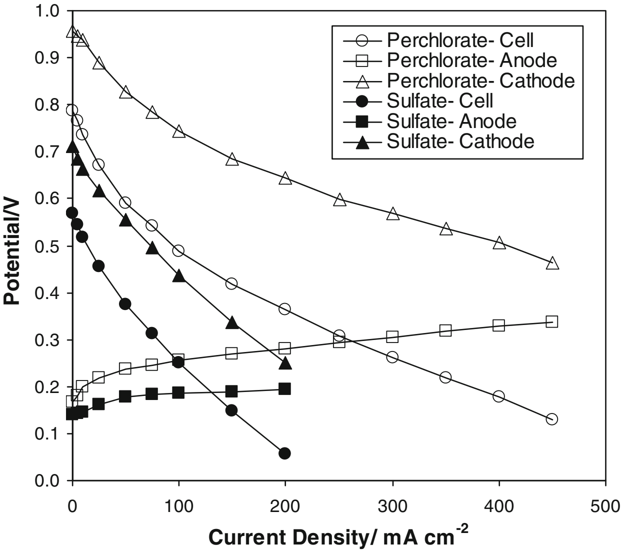

**Fig. 4** Cell and individual electrode polarization (IR-corrected) for a DMRFC supplied with **a** 2.5 M $Fe(ClO_4)_3$ catholyte and 1 M $CH_3OH$, 0.2 M $HClO_4$ anolyte (perchlorate system, $R_{cell} = 0.11\ \Omega\ cm^2$) and **b** 1 M $FeNH_4(SO_4)_2$/0.5 M $H_2SO_4$ catholyte and 1 M $CH_3OH$, 0.1 M $H_2SO_4$ anolyte (sulfate system, $R_{cell} = 0.12\ \Omega\ cm^2$) (90 °C cell temperature, Nafion® 112 membrane, 1 mL $min^{-1}$ anolyte flow rate, 2 mL $min^{-1}$ catholyte flow rate)

is almost certainly a primary factor as the authors have previously observed the effect of anode depolarization due to crossover of ferric ions and the ferric ion concentration is significantly higher in the perchlorate system (2.5 vs. 1 M in the sulfate system).

These non-optimized fuel cell results clearly demonstrate the advantages of using an iron perchlorate salt in the catholyte of a DMRFC rather than a sulfate-based iron salt. The benefits arise primarily due to the increased solubility limit of the $Fe^{2+}/Fe^{3+}$ redox couple (>2.5x) and the increased half cell potential of the $Fe^{2+}/Fe^{3+}$ redox couple (>200 mV). The higher catholyte charge density and better overall cell performance of the iron perchlorate system indicate it is a better choice for the methanol DMRFC.

A wide range of anolyte fuel concentrations can be tested in the DMRFC since the selective nature of the redox couple cathode eliminates the issue of cathode depolarization after fuel crossover. The DMRFC polarization behaviour for methanol concentrations in the range of 2–24 M is shown in Fig. 5. For these experiments, the anolyte included 0.5 M $H_2SO_4$ and the catholyte was comprised of 0.81 M $FeNH_4(SO_4)_2$, 0.09 M $FeSO_4$ and 0.5 M $H_2SO_4$. The optimal fuel concentration is shown to be 16.7 M $CH_3OH$, which agrees with stoichiometry as this concentration corresponds to an equimolar mixture of methanol and water (in 0.5 M $H_2SO_4$). It is likely that at low and high fuel concentrations the anode reaction kinetics are negatively affected by the reduced fuel and water concentration, respectively. It is surprising that the DMRFC can operate at 24 M $CH_3OH$, which represents pure methanol with 0.5 M $H_2SO_4$. The water needed for the anode reaction is obtained in this case by water crossover from the aqueous catholyte.

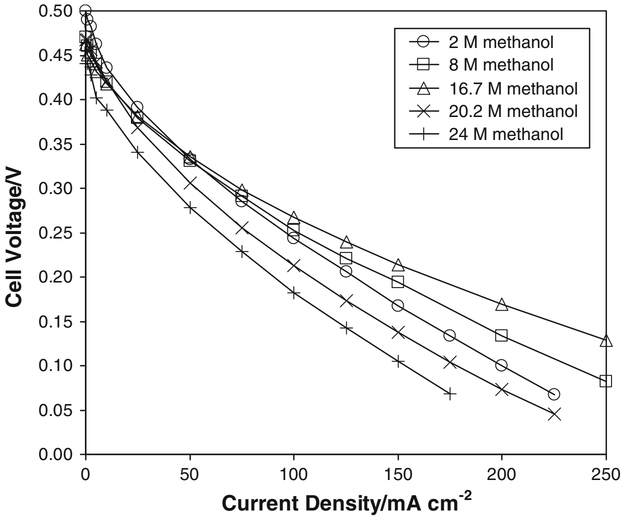

**Fig. 5** Cell polarization curves (IR-corrected) for a DMRFC using anolytes with different methanol concentrations (70 °C cell temperature, Nafion® 112 membrane, X M $CH_3OH$/0.5 M $H_2SO_4$ anolyte, 5 mL $min^{-1}$ anolyte flow rate, 0.81 M $FeNH_4(SO_4)_2$/0.09 $FeSO_4$/ 0.5 M $H_2SO_4$ catholyte, 5 mL $min^{-1}$ catholyte flow rate)

The DMRFC performance at 50, 70 and 90 °C is shown in Fig. 6. In this case the anolyte consisted of 1 M $CH_3OH$ and 0.2 M $HClO_4$ whereas the catholyte was 2.5 M $Fe(ClO_4)_3$. The results clearly show that the DMRFC performs best at 90 °C. Cell temperatures exceeding 90 °C were not tested to avoid electrolyte boiling. The performance improvements observed at elevated cell temperatures are likely due to enhanced reaction kinetics, diffusion rates and/or membrane/electrolyte conductivity.

Short-term DMRFC durability testing was performed galvanostatically at 50 mA $cm^{-2}$ for three different configurations: (1) A perchlorate-based DMRFC at 50 °C, (2) A perchlorate-based DMRFC at 90 °C and (3) A sulfate-based DMRFC at 90 °C. The results are shown in Figs. 7a–c. Linear approximations of the voltage versus time curves show that the DMRFC degrades at approximately 2.3, 2.5 and 3.2 mV $h^{-1}$ for cases (1), (2) and (3), respectively, over this time period. Similarly, the cell impedance increased at a rate of approximately 4.6, 9.3 and 0.9 mΩ $h^{-1}$ for cases (1), (2) and (3), respectively. It is interesting to note that the sulfate-based DMRFC at 90 °C showed the greatest voltage degradation rate but the lowest rate of increase for the cell impedance. Loss mechanisms unrelated to the cell impedance (e.g., accumulation of adsorbates on electrodes) are evidently significant factors in the voltage degradation characteristics for the DMRFC. Although the data in Fig. 7 does not specifically show how

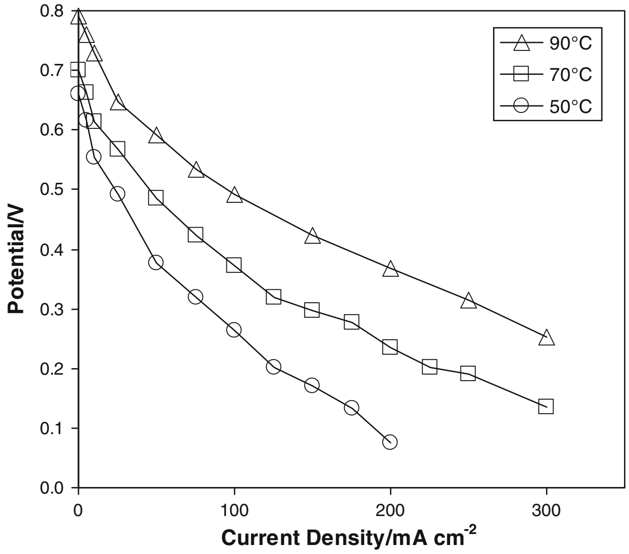

**Fig. 6** Cell polarization curves (IR-corrected) for a DMRFC at different temperatures. (Nafion® 112 membrane, 1 M $CH_3OH$/0.2 M $HClO_4$ anolyte, 1 mL min$^{-1}$ anolyte flow rate, 2.5 M $Fe(ClO_4)_3$ catholyte, 2 mL min$^{-1}$ catholyte flow rate)

the ferric concentration affects the rate of proton displacement in the membrane, it is likely that this phenomenon is plays an important role in the membrane degradation characteristics. One would expect that the higher ferric concentration in the perchlorate system would lead to a greater equilibrium concentration of ferric in the membrane, compromising its proton conductivity. Current interruption (0 mA cm$^{-2}$ for 10 s) after 3.5 h of operation did not have any notable effect on the DMRFC voltage degradation. Overall, the short-term durability tests demonstrate that the DMRFC performance is stable over the 4 h time period.

## 4 Conclusions

Electrolyte composition and cell temperature studies were performed to identify opportunities to improve the performance of the DMRFC. In one set of experiments, redox electrolytes prepared with $Fe(ClO_4)_3$ or $Fe(NO_3)_3$ were considered for DMRFC employment as a substitute for the

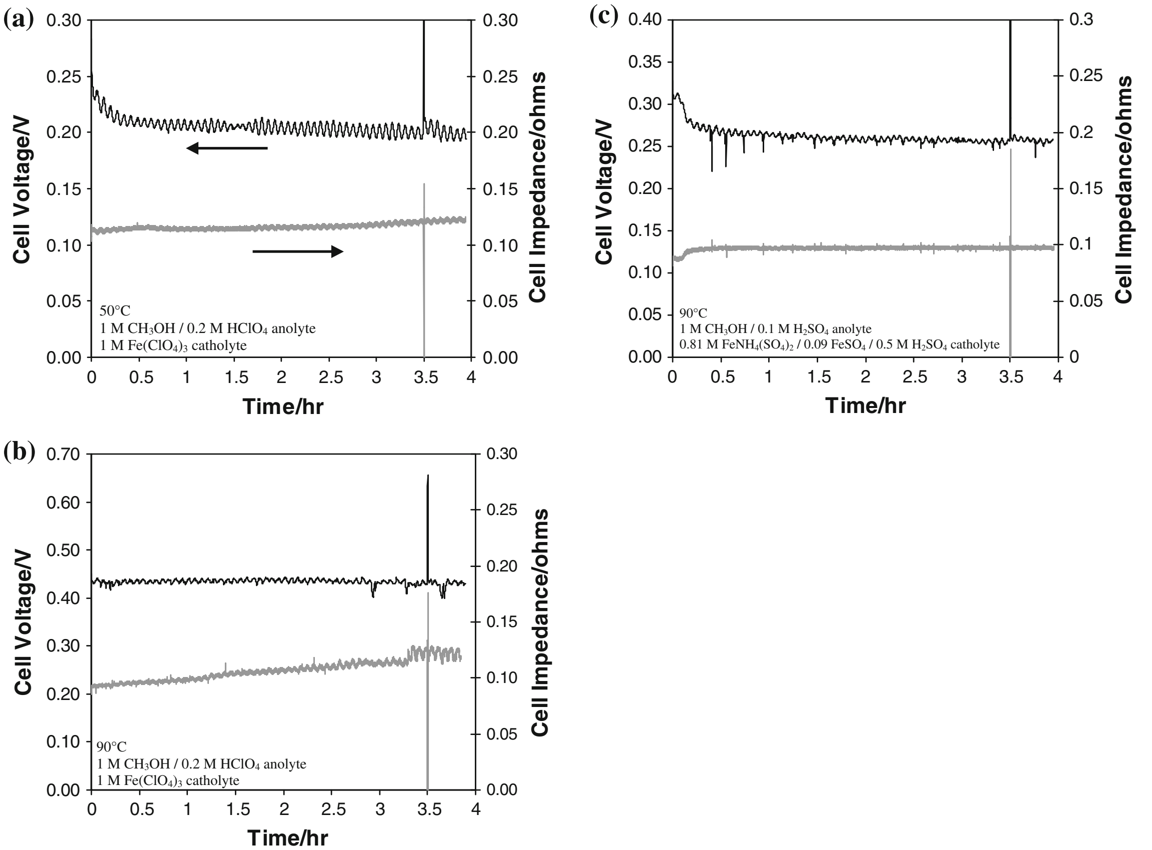

**Fig. 7 a–c** Short-term durability testing and cell impedance measurements for a DMRFC operating galvanostatically at 50 mA cm$^{-2}$ (Nafion® 112 membrane, 1 mL min$^{-1}$ anolyte flow rate, 2 mL min$^{-1}$ catholyte flow rate). A current interruption for 10 s (0 mA cm$^{-2}$) was introduced after 3.5 h

$FeNH_4(SO_4)_2$ catholyte in order to improve the catholyte charge density (i.e., solubility) and electrochemical performance. Electrolyte conductivity measurements, cyclic voltammetry and DMRFC testing were used to evaluate the electrolytes. The $Fe(ClO_4)_3$ catholyte was determined to be a more suitable candidate than the $FeNH_4(SO_4)_2$ catholyte due to its significantly higher solubility (>2.5 vs. ~1 M), increased electrochemical activity, superior electrochemical reversibility and higher observed half-cell potential (0.83 V vs. SHE as opposed to 0.64 V vs. SHE at 90 °C). The advantageous properties of the $Fe(ClO_4)_3$ catholyte became apparent through the increased DMRFC peak power density (79 mW $cm^{-2}$) relative to that observed for the $FeNH_4(SO_4)_2$ catholyte (25 mW $cm^{-2}$). Anolyte composition studies demonstrated optimal fuel cell performance at 16.7 M $CH_3OH$ (equimolar $H_2O/CH_3OH$) for the configuration studied. DMRFC temperature sensitivity tests indicated that maximizing the cell temperature (while respecting the anolyte and catholyte boiling points) delivers the best fuel cell performance. Short-term fuel cell durability tests confirmed stable DMRFC performance for a range of operating conditions. Further advancements in DMRFC technology are anticipated with future experiments targeted towards improving the membrane conductivity, reducing $Fe^{2+}/Fe^{3+}$ crossover and exploring novel cell and electrode designs.

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