Direct oxidation of jet fuels and Pennsylvania crude oil in a solid oxide fuel cell

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Abstract

A Cu-ceria solid oxide fuel cell (SOFC) is shown to generate electric power using jet fuels and Pennsylvania crude oil through direct oxidation of the fuels. The liquid fuels contained up to 910 ppm of sulfur and were injected into the anode compartment either with or without N_2 dilution. The performance of the fuel cell was stable over 30 h for jet fuels and Pennsylvania crude oil without N_2 dilution whereas N_2 dilution prolonged the stable power generation up to 100 h for jet fuel and up to 80 h for Pennsylvania crude oil. The generated power density was about $0.1\,W\,cm^{-2}$ for both fuels.
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1. Introduction

Fuel cells have been extensively investigated for their efficiency in power generation. Among the major types of fuel cells, solid oxide fuel cells (SOFC) differ from others in the electrochemical process. In a SOFC, O_2 is reduced to O^{2-} anions at the cathode before the anions migrate to the anode through a solid electrolyte. The oxidation of the H_2 gas at the anode produces electrons, which forms an electricity generating circuit with the cathode. SOFCs, however, need to operate at high temperatures ($>500\,°C$) where solid electrolytes (usually yttria-stabilized zirconia, YSZ) become ionic conductors. The high-operating temperature may allow direct oxidation of hydrocarbon fuels. Some success in direct oxidation of light hydrocarbons has been reported with methane [1–3] and natural gas [2]. Until the recent development of the Cu-ceria anode SOFC, direct oxidation of heavier hydrocarbons had not been possible primarily because of coke formation [4].

It has been demonstrated that the ability of the Cu-ceria SOFC in the direct oxidation of hydrocarbon fuels without reforming is due to the stability of the anode towards coke formation. This ability to avoid coke formation is a result of

the synergetic roles of Cu and ceria employed in the composite anode present in the SOFC [5,6]. The SOFC has since been shown to generate electric power using a number of fuels other than H_2. These include gaseous fuels, methane [3,7], butane [3,4], ethane [3], butene [3] as well as liquid fuels, hexane [3], *n*-decane [8], toluene [3,4,8], synthetic diesel [8] and gasoline [5], although the liquid fuels need N_2 for dilution. Undiluted *n*-decane was found to cause condensation of the effluent within the fuel cell system making the operation of the fuel cell impossible after 1.5 h [8]. The performance with undiluted diesel showed a gradual decline in power density over 2 h although N_2 flashing restored the performance. The SOFC was also capable of handling undiluted toluene if the ceria in its anode was doped with samaria [3]. Along with the success in direct oxidation of some heavy hydrocarbon fuels, the SOFC was also found to tolerate a reasonable amount of sulfur in a liquid fuel [9]. It generated stable electric power on *n*-decane that contained 100 ppm sulfur, despite the fact that 5000 ppm sulfur rapidly poisoned the anode. The poisoned anode could, however, be restored by flowing steam through the anode compartment.

To further explore the potential of the Cu-ceria SOFC, less processed fuels, such as jet fuels and crude oil, that contain fairly high levels of sulfur were used. Pennsylvania crude oils have important characteristics that make them more amendable to use in a SOFC than other types of oils. In particular, the oil is very low in asphaltic content, with

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very low nitrogen and sulfur [10]. The oil is dominated by *n*-alkanes with some cycloalkanes [11]. A useful summary of data on this oil is provided in the standard text by Levorsen [12]. In the early years of the petroleum industry, Pennsylvania crudes enjoyed an economic advantage, for several reasons. These oils provided high-distillation yields (up to 60%) of valuable gasoline and kerosene [10]. The heavier hydrocarbons made superb lubricating oils, having very high-viscosity indices (i.e. an indication that the oil would not become too thin at high temperatures, nor too thick at low temperatures) [13]. However, as refiners learned to handle aromatic, high-sulfur crudes the relative chemical purity of the Pennsylvania crude was no longer a special advantage. Further, the development first of lubricating oil additives and then of synthetic lubricating oils reduced or eliminated the advantages of Pennsylvania crude as a source of lubricating oil. Thus, there is interest among producers of this oil to find new applications. Use in a SOFC could capitalize on the highly paraffinic nature of the oil (being not so likely to coke on the fuel cell as aromatic or asphaltic oils) and on the low-sulfur and -nitrogen contents.

Recently, there has been some interest in possible application of SOFCs on jet aircraft [14]. Among several possible applications are the use of fuel cells to cabin pressurization and anti-icing systems, replacing the pneumatic systems currently used. This concern, combined with our own interest in developing the next generation of advanced jet fuel [15–17] led us to investigate the possible application of jet fuel in the same type of fuel cell. Some of the promising results are reported herein.

2. Experimental

The SOFCs were prepared using the methods developed by the researchers at the University of Pennsylvania [6,18,19]. The fuel cell consisted of a cathode, a dense electrolyte and a porous anode. The dense layer of YSZ (Tosoh TZ-8Y), 60 μm thick, was dual cast along with the anode of YSZ, 400 μm thick, in which pore formers, PMMA (Scientific Polymer Products Inc., 100–300 mesh) and graphite (Alfa 325 mesh), were incorporated. Wafers of YSZ were

sintered by firing the cast discs at 1550 °C for 4 h. The cathode was then pasted onto the dense electrolyte layer with a 50:50 mixture of YSZ and LSM ($La_{0.8}Sr_{0.2}MnO_3$, Praxair Surface Technologies) and then calcinated at 1250 °C for 2 h. Cu and ceria were the last to be added to the porous YSZ layer via wet impregnation of aqueous solutions of $Cu(NO_3)$ (Fisher Scientific Co, 98%) and $Ce(NO_3)$ (Alfa, 99.5). The impregnated discs were then given a heat treatment at 500 °C for 2 h to transform the nitrides into oxides. The impregnation/heat treatment often needed to be carried out more than once in order to get the required amounts of ceria (10 mass%) and Cu (20 mass%) into the porous YSZ layer. A Pt mesh and an Au ring were employed as the current collector and attached to the cathode and the anode using Pt ink and Au ink, respectively. Pt wire and Au wire were then attached to the Pt mesh and Au ring correspondingly for electronic conduction. The fuel cells were sealed onto alumina tubes using a zirconia-based adhesive (Aremco, Ceramabond 552). The fuel cells had an active anode surface area of $0.2 \, cm^2$.

Fig. 1 is the schematic of the experimental set-up for the SOFC and the liquid fuel injection. Both gaseous and liquid fuels can be used in this fuel cell system. Liquid fuels are injected into a thicker stainless tube (1/8 in. o.d.) through a thinner (1/16 in. o.d.) tube where the temperature was predetermined to be about 350 °C. The liquid fuels were expected to vaporize before reaching or being brought to the anode of the fuel cell by means of the flowing N_2 in the thicker tubing. If gaseous fuels, such as H_2 or butane, are used, the syringe pump is removed and the end is blocked. All the experiments were conducted at 973 K.

The crude oil used in this study was Pennsylvania crude oil obtained from Well 64, Warren, PA, USA, with Glade formation. The oil was used without any further processing. The GC-MS spectrum of the oil is shown in Fig. 2 and the oil contained 910 ppm of sulfur. The jet fuels JP-8 Plus and JP-7 were obtained from the US Air Force, Dayton, OH, USA. The GC-MS spectrum of the jet fuels are presented in Figs. 3 and 4, respectively. Sulfur contents were 475 ppm for JP-8 Plus and 10 ppm for JP-7. All sulfur contents were determined by IR absorption using a LECO SC-132. When nitrogen was used to dilute and bring the
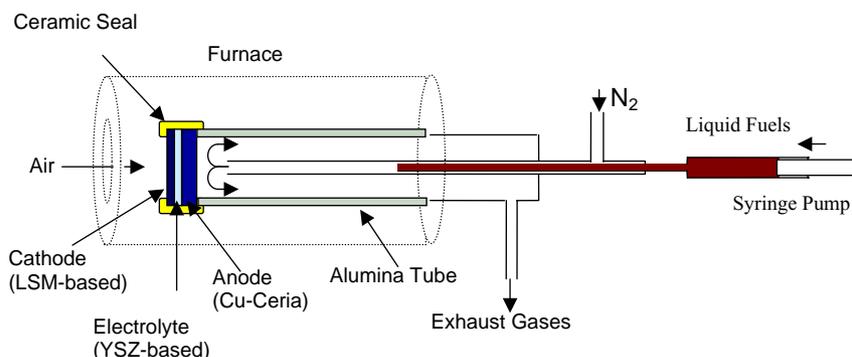

Fig. 1. Schematic of the experimental set-up for the Cu-ceria SOFC running on a liquid fuel.
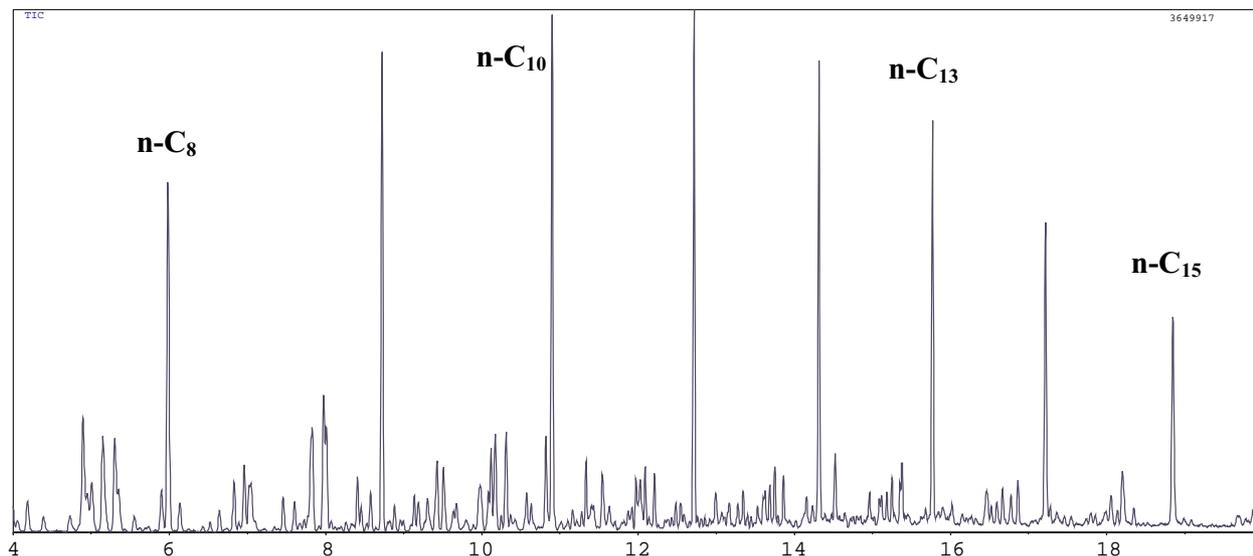
Fig. 2. GC-MS spectrum of the Pennsylvania crude oil.
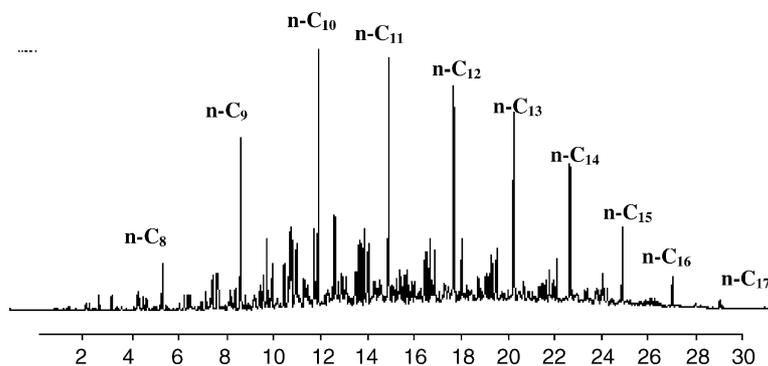

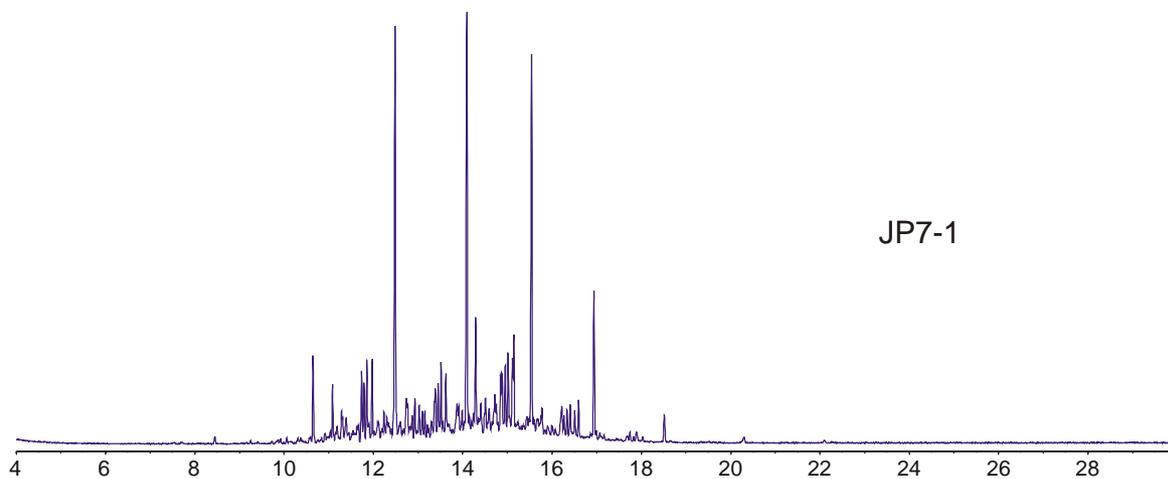Fig. 3. GC-MS spectrum of the JP-8 Plus jet fuel.

Fig. 4. GC-MS spectrum of the JP-7 jet fuel.

vapor of the fuels to the anode, the proportion of the fuels was given in mass percentage. This was worked out using ambient temperature densities of each fuel against that of nitrogen. The densities of the fuels were experimentally determined with the crude oil being $0.8195\,\mathrm{g\,cm^{-3}}$ and the jet fuel being $0.8364\,\mathrm{g\,cm^{-3}}$, whereas the density of nitrogen was taken as $1.251 \times 10^{-3}\,\mathrm{g\,cm^{-3}}$ from the supplier.

3. Results and discussion

First, it was proved that the fabricated fuel cells can show a performance comparable to the results previously reported on H_2 and butane. The fuel cell initially showed a poor performance on H_2. However, a significant improvement was observed after butane was run on the fuel cell. This observation directly correlates with work done at the University of Pennsylvania, which discusses possible reasons for the improved performance after running butane through the fuel cell [4,6,20]. The performance of the fuel cell on hydrogen after running butane is quite similar to the reported results, and can be viewed in Figs. 5 and 6, where it is displayed as a part of fuel concentration distributions [4,8].

When the jet fuel was used at different concentrations, the open circuit voltages (OCV) were about 0.8 V, as shown in Fig. 5. The OCVs were substantially lower than that of H_2 but similar to that reported for toluene [8] and marginally lower than other hydrocarbon fuels, such as butane [3,4] and methane, ethane, hexane, etc. [3]. Analogous results were obtained with the Pennsylvania crude oil as given in Fig. 6. The low OCVs might be associated with the fact that

the hydrocarbons are electrochemically oxidized. There are actually a number of surface reactions taking place during the electrochemical oxidation and the determining reaction might have a low OCV. Excellent discussions on this can be found in Refs. [3,4,21]. In addition, the OCV for both the jet fuel and the Pennsylvania crude oil appeared to vary consistently with the concentration of the fuels, with a low concentration having a lower OCV. This was not observed when Cu-ceria SOFC was run on toluene [3]. The maximum current density for both fuels also increased with increasing concentration with the maximum current density of about $0.7\,A\,cm^{-2}$ at 65 mass% being similar to that reported for 55 vol.% of toluene [3].

The long-term performance of the fuel cell on jet fuel JP-8 Plus is shown in Fig. 7, whereas that of the Pennsylvania crude oil is illustrated in Fig. 8. Both fuels were injected into the anode compartment at a rate of $0.02\,ml\,min^{-1}$. The undiluted jet fuel and crude oil each generated power of about $0.1\,W\,cm^{-2}$ stably over about 30 h before a steady decline in the performance was observed. It is worth noting that a rapid decline in power density was seen in the first 2 h or so before stabilization was reached. This was thought to be
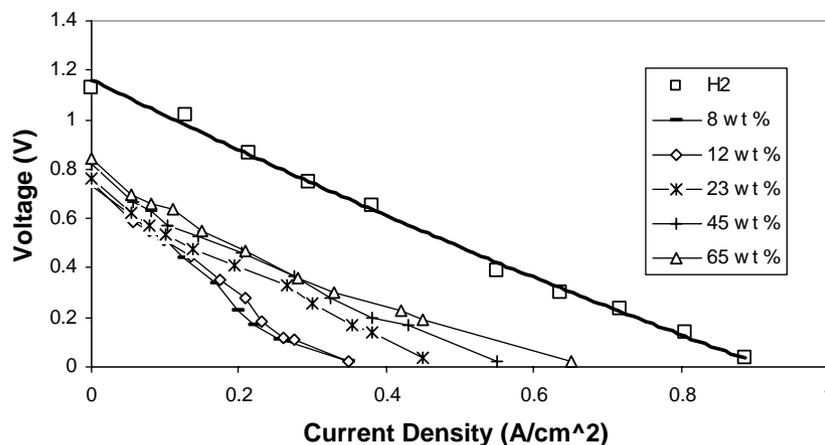

Fig. 5. Potential vs. current density for Cu-ceria SOFC fueled by the JP-7 jet fuel with different concentrations at 973 K.
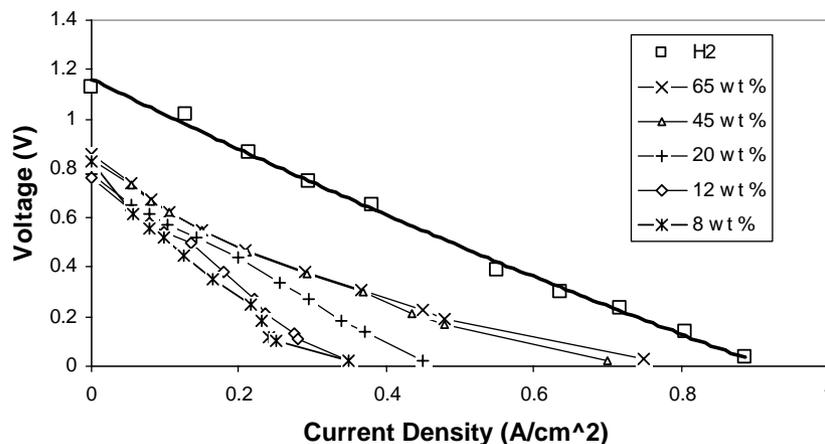

Fig. 6. Potential vs. current density for Cu-ceria SOFC fueled by the Pennsylvania crude oil with different concentrations at 973 K.
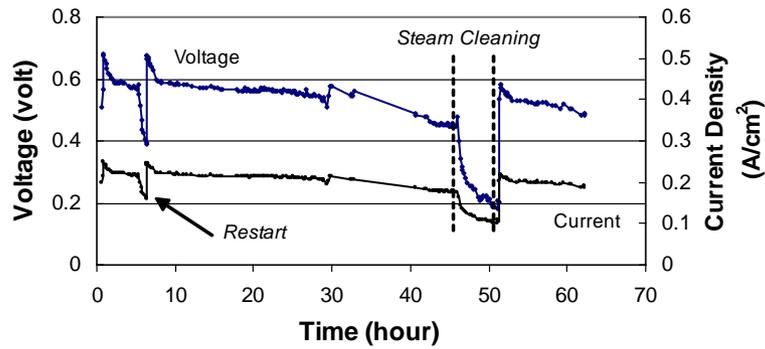
Fig. 7. Potential and current density vs. time for undiluted jet fuel JP-8 Plus at 973 K.
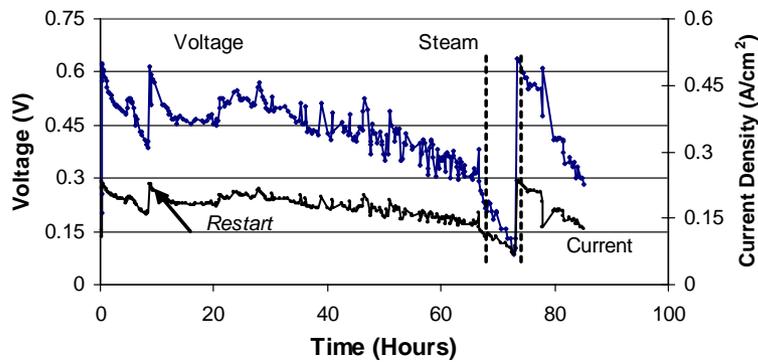

Fig. 8. Potential and current density vs. time for undiluted Pennsylvania crude oil at 973 K.

the transient behavior, possibly caused by a slow establishment of the chemical structure of the hydrocarbon layer that takes place within the anode, as discussed previously [20]. This transient behavior was explored further by deliberately shutdowning and restarting the fuel. A similar transient was found in both fuels. The transient behavior might account for the rapid degradation in the performance of the fuel cell operated on undiluted diesel reported before [9].

There are two possible causes of degradation of the performance of the fuel cell. One is the sulfur contained in the fuels [9] as both the crude oil and jet fuel contained a substantial amount of sulfur. It has already been demonstrated that the Cu-ceria SOFC operated stably over 100 h on n-decane

that contained 100 ppm of sulfur in thiophene, however, 5000 ppm of sulfur dramatically degraded the performance of the Cu-ceria SOFC even though the performance could be restored with steam [9]. However, the fuel cell displayed a similar degradation after about 40 h when operated on jet fuel JP-7 which had a sulfur content of 10 ppm (Fig. 9) as well. The high-sulfur content in JP-8 Plus and the Pennsylvania crude oil, therefore, might not be the cause for the performance decline.

The other likely cause is still coke formation inside the anode. Cu-ceria fuel cell has been proven to be resistant to coking but its enduring resistance has not been examined since the experiments conducted on undiluted fuels mostly
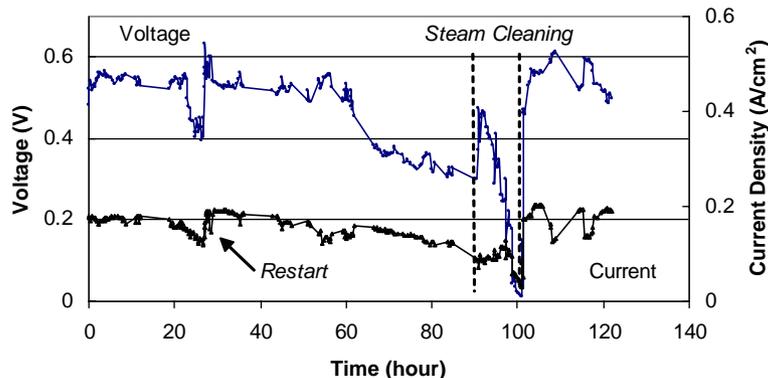

Fig. 9. Potential and current density vs. time for undiluted jet fuel JP-7 at 973 K.
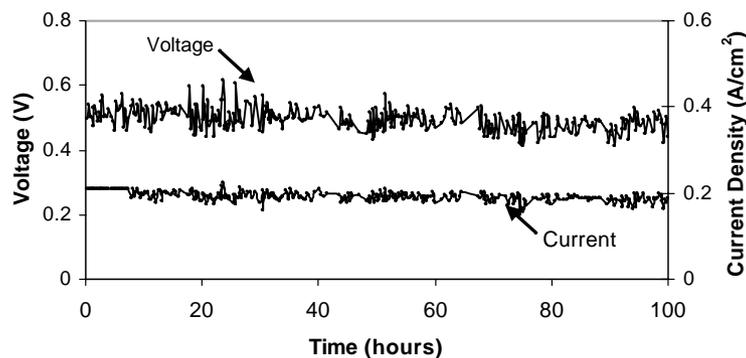
Fig. 10. Potential and current density vs. time for diluted jet fuel JP-8 Plus at 973 K.
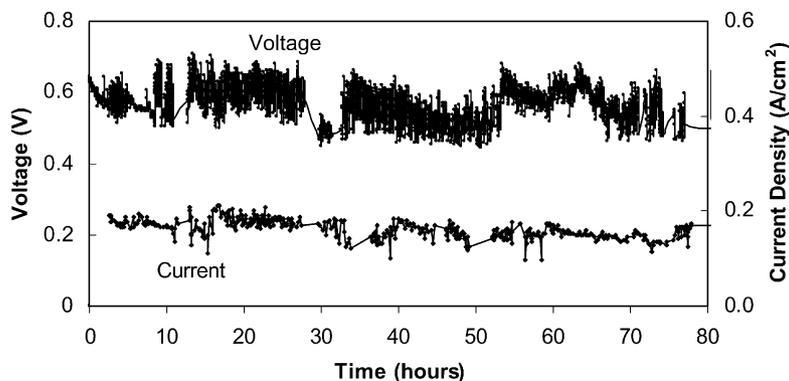

Fig. 11. Potential and current density vs. time for diluted Pennsylvania crude oil 973 K.

lasted for just hours. Even in the relatively quick tests, the performance was still found to deteriorate as a result of tar formation [3,8]. It may be argued that aromatics contained in the jet fuels and Pennsylvania crude oil might be the cause for coking or the degradation. However, our study showed that the fuel cell stably operated on undiluted toluene for more than 30 h too. Therefore, the coking may just result from slow carbon deposition, which gradually deteriorates the performance of the fuel cell. Nevertheless, the degraded performance of the fuel cell could be completely restored by flushing the fuel cell with steam (50% in N_2) for a few hours as illustrated in Figs. 7–9. Steam is known to assist decomposition of coke/tar and the steam flushing might have assisted in the dissolution of the coke/tar into gases. The anode was activated again as a result. Under the current design of the fuel cell and in the employed experimental conditions, the conversion of the fuels was only about 1–3% as previously discussed [8,9]. Such a high level of unconsumed hydrocarbon fuels would promote coking in the anode compartment. Dilution of the fuel by varying the experimental conditions may lead to less or no coking. Dilution of the fuels with N_2 was simple and an investigation was conducted.

When nitrogen was used to dilute the jet fuel, JP-8 Plus, and the crude oil, a more stable performance was observed as shown in Figs. 10 and 11, respectively. Both the jet fuel and the crude oil were supplied at $0.030\,\mathrm{ml\,min^{-1}}$, with a fuel concentration of 40 mass%. Only marginal decline in power potential and current density was observed over 100 h for

the jet fuel and nearly 80 h for the crude oil. The generated power density was also about $0.1\,\mathrm{W\,cm^{-2}}$ in both cases, similar to the power density generated on undiluted jet fuel (Fig. 7) or crude oil (Fig. 8) as well as N_2 diluted decane, toluene, synthetic diesel [3], and undiluted gasoline reported previously [5]. It should also be mentioned that both voltage and current density fluctuated with voltage showing a greater oscillation. Similar fluctuation was seen in undiluted jet fuel and crude oil and reported for toluene [3] or gasoline [5] although the extent for the diluted crude oil and jet fuel was more pronounced. The exact cause of the fluctuation is not known but might be related to the interruptions of the nitrogen gas to the equilibrium diffusion layers at certain reaction surfaces within the anode compartment. However, the improved stability of the fuel cell performance clearly demonstrated the influence of fuel dilution. This dilution effect can be readily achieved by reducing the fuel supply rate and improving the fuel cell design to obtain an increased conversion rate. With these improvements, the Cu-ceria fuel cell is anticipated to operate stably on heavy hydrocarbon fuels for a lengthy period of time.

4. Conclusions

The Cu-ceria SOFC is shown to be capable of generating electric power using less processed fuels, such as jet fuels and Pennsylvania crude oil, containing sulfur up to

910 ppm. It generates stable power of 0.1 W cm^{-2} for up to 30 h on both the jet fuels and the Pennsylvania crude oil. When nitrogen was used to dilute the jet fuels and crude oil, only a marginal decline in power potential and current density was observed over 100 h for the jet fuel and nearly 80 h for the crude oil. The generated power density was also about 0.1 W cm^{-2} in both cases, similar to the power density generated on the undiluted fuels. Therefore, with improvements in the design and experimental conditions, the Cu-ceria SOFC may operate on heavy hydrocarbon fuels to generate electric power stably over a long period.

Acknowledgements

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