Short communication

Direct oxidation of waste vegetable oil in solid-oxide fuel cells

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Abstract

Solid-oxide fuel cells with ceria, ceria-Cu, and ceria-Rh anode were demonstrated to generate stable electric power with waste vegetable oil through direct oxidation of the fuel. The only pre-treatment to the fuel was a filtration to remove particulates. The performance of the fuel cell was stable over 100 h for the waste vegetable oil without dilution. The generated power was up to $0.25\,\mathrm{W\,cm^{-2}}$ for ceria-Rh fuel cell. This compares favorably with previously studied hydrocarbon fuels including jet fuels and Pennsylvania crude oil.
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1. Introduction

Solid-oxide fuel cell, SOFC operates at high temperatures ($>500\,^\circ\mathrm{C}$) at which 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 ceria-Cu anode SOFC, direct oxidation of heavier hydrocarbons had not been possible primarily because of coke formation [4].

The ability of ceria-Cu 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 essentially attributed to ceria employed in the composite anode in the SOFC [5,6]. The SOFC has been demonstrated to generate electric power using a number of hydrocarbon fuels. These include gaseous fuels, methane [3,7], butane [3,4] as well as liquid fuels, hexane [3], *n*-decane [8], toluene [3,4,8], synthetic diesel [8] and gasoline [5]. 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]. The ceria-Cu-based SOFC 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. More recently, less processed logistic jet fuels, and even Pennsylvania crude oil were used to generate stable electric power using a similar SOFC with the fuels containing as high as 910 ppm of sulfur [10].

Waste cooking oils are generated locally wherever food is cooked or fried in oils. These can be derived from corn, palm, cottonseed, soy or any of a wide variety of plant sources. These oils might even be mixed in operations where oils are not standardized but purchased based on cost. In addition, there are waste animal-derived oils and fats as a result of cooking that represent potential fuel sources. The utilization of used vegetable oils represents the application of a waste by-product that other than filtration, does not require further post-processing and should be considered as an advantageous approach. This is different from conversion of a triglyceride first to biodiesel via transesterification, only to then consume the material as fuel. The process of transesterification requires an extra step from raw material to fuel cell feedstock. This uses energy in the form of labor and process heat and requires at least a small processing plant. The approach taken in this paper is filtration of the fuel source to remove particulate matter followed by direct use in the fuel cell. These naturally occurring oils are free of most of the contaminants found in fossil energy sources such as petroleum,

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shale oil or coal-derived liquids. Nickel and vanadium are absent and sulfur is in amount of 2–5 ppm. Nitrogen is also essentially absent.

It was the aim of this study to examine if waste vegetable oil can be used as fuel for SOFC. Ceria-based anodes were used in the SOFC. It is known that ceria is one of the best oxidation catalysts among oxides although its catalytic activity is not comparable to that of some metallic catalysts [11,12]. In addition to ceria and ceria-Cu anode, precious metal catalyst Rh was added to ceria anode. Their performance on the direct oxidation of waste vegetable oil was examined and some of the promising results are reported herein.

2. Experimental

The preparation of SOFCs was described in details elsewhere [10]. Briefly, the fuel cell device 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 1823 K 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 1523 K for 2 h. Cu, ceria and Rh 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%), $Ce(NO_3)$ (Alfa Aesar, 99.5%), and $Rh(NO_3)_3$ (Alfa Aesar 13.97%). The impregnated discs were then given a heat treatment at 773 K 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 wt%) and Cu (20 wt%) into the porous YSZ layer. The Cu or Rh oxides were reduced to metallic Cu and Rh *in situ* upon exposure to reducing atmosphere at high temperatures when the SOFC is operated. The details of the metal oxide reduction process have been extensively discussed [5]. Three different anodes were hence prepared and their performance on a SOFC was evaluated individually. These anodes included ceria only, ceria-Cu, and ceria-Rh. The ceria only anode contained no Cu or Rh whereas ceria-Cu and ceria-Rh were impregnated with 20 wt% Cu or 1 wt% Rh, respectively. The ceria residing over the porous YSZ surface is the catalyst while Cu provides electronic conductivity [4–6]. Rh is a noble metal catalyst and added to enhance the catalysis of ceria anode. Its role in ceria-based anode was also studied and discussed elsewhere [11].

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 cm². The liquid fuels of interest were supplied to the fuel cell by a New Era Pump NE 1000 through one 16 in. o.d. steel tube. The fuel supply rate was varied by controlling the flow rate of the pump. The fuels were
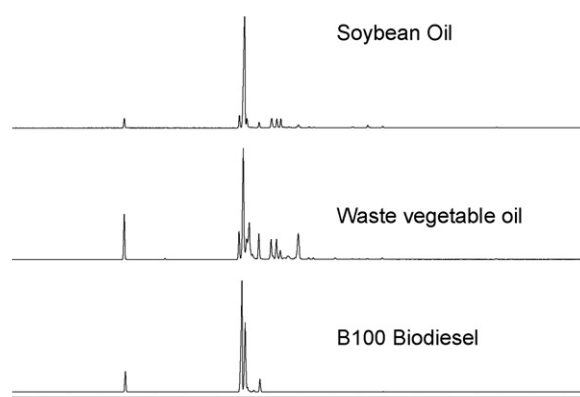

Fig. 1. GC–MS spectra of the waste vegetable oil compared to soybean oil and B100 biodiesel.

expected to vaporize before reaching the anode of the fuel cell. All the experiments were conducted at 973 K.

The oil was obtained from a local fast-food restaurant without any processing steps. The sample was transferred directly from a frying unit to the container. This brown-black oil ($\sim$2000 g) was filtered warm through a column of alumina (300 g) into a clean container. This filtered oil, a pale amber liquid, was used directly as the fuel source for the described above SOFC.

The filtered waste vegetable oil was co-injected (1 μl of each diluted sample (10 mg ml^{-1} in dichloromethane) and tetramethylammonium hydroxide (TMAH) (25%, w/w in MeOH) into the injector port of a gas chromatography/mass spectrometry (GC/MS) apparatus [13]. The injector was at temperature of 300 °C, which is a sufficient reaction temperature for hydrolysis and conversion of a triglyceride to the methyl ester of the fatty acid. The chromatograms of the waste vegetable oil, soybean oil and B100 biodiesel (methyl soyate) are shown in Fig. 1. The results show that the waste vegetable oil is essentially all triglyceride, with perhaps some oxidation products, as expected. The waste vegetable oil contained 2.33 ppm of sulfur presumably from sulfur-containing amino acids in the proteins cooked in the oil.

3. Results and discussion

Fig. 2 shows the voltage–current density (*V–I*) and power density–current density (*P–I*) performance curves for the fuel cell with ceria only anode at 973 K, which was fueled with the waste vegetable fuel at three different supply rates, 1, 5, 20 μl min^{-1}. Open circuit voltages (OCV) were in the range of 0.85–0.95 V, with a higher supply rate, giving rise to higher OCV. The OCVs were substantially lower than that of H_2 but similar to that reported for jet fuel [10], toluene [8] and marginally lower than other gas hydrocarbon fuels such as butane [3,4]. The maximum power density varied with the fuel supply rate and 110 mW cm^{-2} was obtained with the highest fuel supply rate. It is noted that at the lowest flow rate, voltage and power density display a rapid decline at a current density greater than 250 mA cm^{-2}.

Fig. 3 exhibits the *V–I* and *P–I* performance curves for the fuel cell with ceria-Cu anode at 973 K, which was fueled with

Fig. 2. Potential and power density *vs.* current density at three different flow rates for ceria only fuel cell at 973 K.
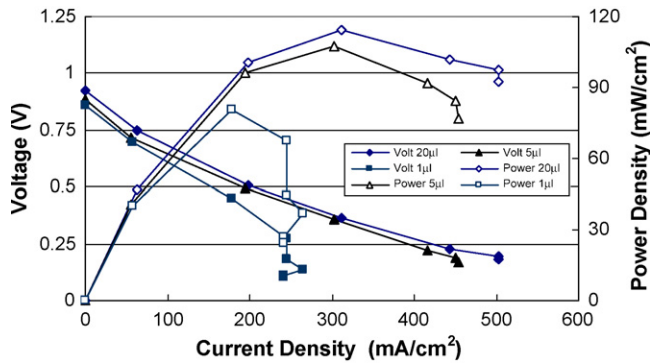

Fig. 4. Potential and power density vs current density at three different flow rates for ceria-Rh fuel cell at 973 K.

the waste vegetable fuel at three different supply rates −1, 5 and 20 μl min^{-1}. The maximum power density was rather similar to that for the fuel cell with ceria only anode at the fuel supply rate of 1 μl min^{-1} and marginally higher at the fuel supply rate of 5 μl min^{-1}. At the fuel supply rate of 20 μl min^{-1}, the maximum power density was considerably low at approximately 30 mW cm^{-2}. The quite different performance of the fuel cell with ceria-Cu anode with respect of the fuel cell with ceria only anode may be associated with the fact that Cu is also a known catalyst for triglyceride [19], the main component contained in the waste vegetable oil (Fig. 1).

First of all, the rapid decline in power density at the fuel supply rate of 1 μl min^{-1} for both fuel cells with ceria only and ceria-Cu anodes might result from concentration resistance that became significant when fuel concentration was too low at this low fuel supply rate, in another word a limiting current was reached. The slightly better performance, shown by the fuel cell with ceria-Cu anode with power density reaching 250 in contrast to 170 mA cm^{-2} before declining at 300 instead of 250 mA cm^{-2} for the fuel cell with ceria only anode, may be attributed to the catalytic effect of Cu on triglyceride. The enhanced breakdown of the waste vegetable may increase the concentration of the total hydrocarbons when the triglyceride decomposed into smaller hydrocarbons. At the intermediate fuel supply rate (5 μl min^{-1}), such catalytic effect was not as significant, the observed power density for the two was hence similar. At the highest fuel supply rate, excessively high concentration
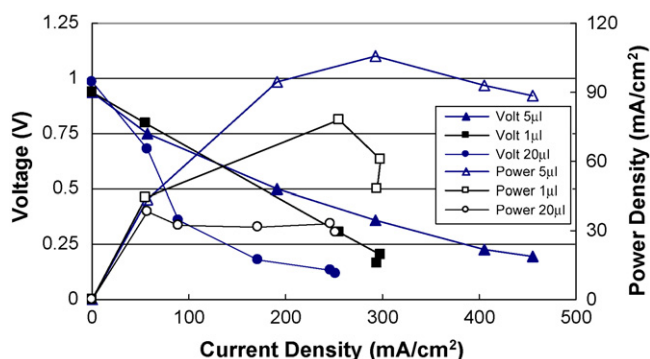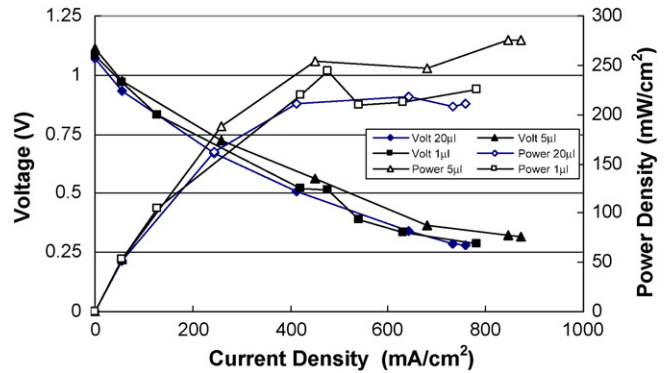
of the hydrocarbons resulted in formation of a dense layer of carbonaceous deposit which would significantly reduce the power density as discussed by He et al. [20]. Comparison of the long-term performance between the fuel cells with ceria only and ceria-Cu anodes, as will be discussed in Figs. 5 and 6, may lend additional support on this explanation. The fuel cell with ceria-Cu anode showed somewhat higher longer power density probably because of Cu catalysis but became deactivated in a shorter period of time mostly likely as a result of quicker formation of carbonaceous deposit.

Fig. 4 presents the *V–I* and *P–I* performance curves for a fuel cell with ceria-Rh anode at 973 K, which was fueled with the same waste vegetable fuel at three different supply rates, 1, 5, 20 μl min^{-1}. OCVs were about 1.1 V and much closer to the Nernst potential. The maximum power densities were also significantly higher than that shown in Figs. 2 and 3 for the corresponding fuel supply rates. A power density of 250 mW cm^{-2} was obtained at fuel supply rate of 1 μl min^{-1}. In addition, voltage and power density showed no rapid decline at current density up to 800 mA cm^{-2}. Rhodium is an excellent catalyst. Its addition would enhance the conversion of the vegetable oil into H$_2$ and CO in the reforming process as well as the oxidation of these gaseous fuels. In addition the noble metal catalyst is reported to improve gas diffusion [14] and hence to reduce concentration resistance. As a result, higher voltage and power densities were obtained with ceria-Rh anode. This might also be the reason that a rapid decline in voltage and power density was not observed in the fuel cell with ceria-Rh anode at fuel supply rate of 1 μl min^{-1}.

The significant performance improvement was somewhat surprising as ceria-Rh anode was found to be effective in enhancing the performance of ceria-Rh fuel cell when the fuels were H$_2$ and CH$_4$ but to a much lesser extent when the fuel cell was fueled with larger hydrocarbons such as C$_4$H$_{10}$ [11]. This ineffectiveness with C$_4$H$_{10}$ was postulated to be the result of carbon saturation on the surface of precious metal catalysts [11]. The waste vegetable oil consists essentially of triglyceride, much larger hydrocarbons, as illustrated in Fig. 1. Rh addition to ceria in the anode should cause limited performance enhancement when the fuel cell operates on the waste vegetable oil according to this rational. This unexpected result may be evidence that will lead to better understanding of the effect of Rh additions.

Fig. 3. Potential and power density *vs.* current density at three different flow rates for ceria-Cu fuel cell at 973 K.

Performance improvement due to precious metal catalyst additions in SOFC remains to be understood. Kendall et al. [17] indicated that there were a number of chemical reactions that could take place within the anode of SOFC fueled by methane. Steam reforming is one of the possible reactions that may take place as a result of Rh additions since all the precious metal catalysts are also steam reforming catalysts. Takeguchi et al. [14] favored this interpretation and suggested that precious metal catalysts enhance fuel cell performance by promoting steam reforming. Steam reforming was, however, considered unlikely by McIntosh et al. [11]. These authors found that the measured OCV as a function of fuel composition of CH_4–CO_2–H_2O did not agree with the calculated potentials for steam reforming of CH_4 to H_2. In addition, they argued that the H_2O:C ratio was also too low for steam reforming. Given that there are many possible reactions and the measured OCVs always lie between the potentials for steam reforming potential and full oxidation, the measured potential may well be a number of reactions that simultaneously take place on the catalyst surface.

The efficiency of a fuel cell operating on waste vegetable is difficult to determine precisely because of the lack of knowledge on the chemical reactions that take place at the fuel cell anode. For example, using *n*-butane as a fuel McIntosh et al. observed a considerably lower OCV than the theoretically calculated one for complete combustion of *n*-butane to CO_2 and H_2O. The authors concluded that an intermediate partial oxidation reaction, probably *n*-butane to *n*-butanal, might have occurred [11,15]. Vegetable oil is comprised of much larger molecules and, therefore, a number of partial reactions are possible. Prior to the identification of the dominant reaction(s), the theoretical OCV cannot be calculated and, therefore, the total efficiency cannot be estimated. However, the fuel utilization can be estimated and are shown in Table 1 below. The theoretical current was calculated based on the fuel supplied while the measured currents were taken from the power density *versus* current density curves at the maximum power densities.

While the utilization rates shown in Table 1 are relatively low, this numbers should not be used for making any conclusions, because the fuel call used in this study was not designed to provide a high utilization rate. Also, the data in Table 1 at the flow rate of 20 µl min^{-1} are comparable to what was reported for *n*-butane fueled SOFCs in Ref. [16].

The long-term performances of the three fuel cells on the waste vegetable oil are exhibited in Figs. 5–7, respectively. The liquid fuel was injected into the anode compartment at a rate of 1 µl min^{-1} in all cases. This fuel generated electric power of about 60 mW cm^{-2} on the ceria only fuel cell (Fig. 5). The
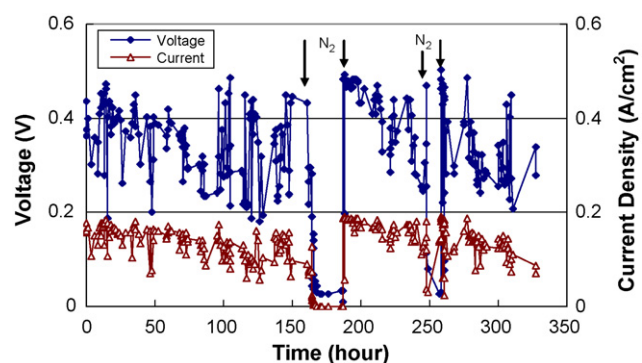

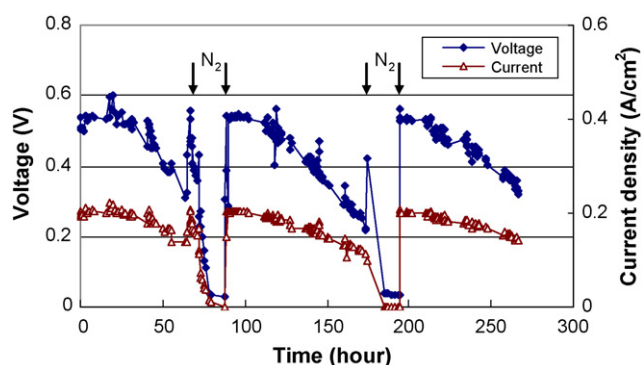Fig. 5. Potential and current density *vs.* time for ceria only fuel cell at 973 K.

Fig. 6. Potential and current density *vs.* time for ceria-Cu fuel cell at 973 K.

electric power generated was stable over about 100 h before a steady decline in the current density was observed. Flushing using N_2 for about 10 h restored the performance and the fuel cell continued to generate power which was stable for about another 40 h before the need for flushing again. The fuel generated a power of about 100 mW cm^{-2} on the ceria-Cu fuel cell (Fig. 6). The power generation was stable for about 30 h before its performance declined with the voltage showing a more significant drop. In comparison with that for ceria only fuel cell, the oscillations in both voltage and current density were less pronounced. Again, the fuel cell could be recovered to its original shape as both the voltage and current density could be restored after N_2 flushing for about 10 h. However, it appears that stable power generation durations became shorter after each flushing. Previous study also indicated that the performance of ceria-Cu fuel cell declined after operating on jet
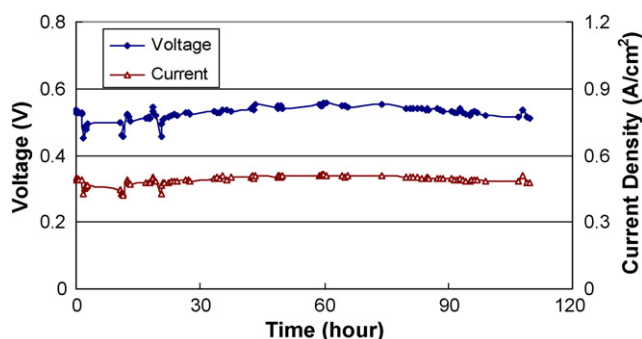
Table 1
Estimated fuel utilization rate (%)

	Flow rate (µl min^{-1})		
	20	5	1
Ce only	0.57	2.20	6.62
Ce-Cu	0.45	2.16	9.38
Ce-Rh	0.76	3.35	17.8

Fig. 7. Potential and current density *vs.* time for ceria-Rh fuel cell at 973 K.

fuels or Pennsylvania crude oil for about 30 h [10]. Cu free fuel cells appear to show more stable performance as demonstrated in Figs. 5 and 7, as well as some of our unpublished work on jet fuel. More detailed discussions on this issue will be presented separately [18].

Electric power of about 250 mW cm^{-2} was generated on the ceria-Rh fuel cell stably over 100 h. Both the voltage and the current density were steady without significant oscillations. The prolonged stability of power generation observed in this fuel cell may be explained as follows. First, the fuel supply rate is low (1 compared with 20 μl min^{-1} [10]). Therefore, there is less carbon deposition which is the major cause of anode deactivation [17]. Second, Rh is more effective oxidation catalyst so that more H_2O and CO_2 are generated that assisted with diluting the fuel and reduced carbon deposition. Third, the vegetable oil contains more than 12% oxygen. The oxygen/carbon ratio of the fuel may also lessen carbon deposition. Hence, one may argue that an oxygen containing fuel will be less efficient as it oxidizes within the anode chamber. However, the heat generated from the oxidation may still be utilized for maintaining the operation temperature. Finally, it should be pointed out that the vegetable fuel contains only a trace amount of sulfur. This is very crucial to the stability of power generation in the fuel cell that has Rh in its anode, as most precious metal catalysts are susceptible to sulfur poisoning. Ceria-Rh fuel cell did not operate for long on a jet fuel that contained 475 ppm sulfur [18].

One of the observations from Fig. 5 is that the voltage fluctuated considerably. This kind of voltage oscillations was observed in ceria-Cu fuel cell that operated on N_2 diluted jet fuel and Pennsylvania crude oil [10]. No attempt has been made to understand the voltage oscillations. One possible explanation is to relate this to the rapid decline of V–I/P–I curves at high current density as displayed in Fig. 2 when the fuel cell was operated at 1 μl min^{-1}. At this low fuel supply rate, the fuel cell operated on the border of rapid voltage/power reduction due to concentration resistance. It is hence suggested that the oscillations observed in the ceria only fuel cell may be associated with concentration resistance. That is when the current density varies slightly it could cause the voltage to decline dramatically, leading to a low voltage. This drop in current density, in turn, brings the voltage back to a higher value. This explanation is consistent with the observations that minimal oscillations were found in ceria-Rh fuel cell when V–I/P–I curve did not show declines as in Fig. 4. In the meantime, the Cu-ceria fuel cell appeared to show some oscillations as its V–I/P–I curve declined.

4. Conclusions

Solid-oxide fuel cells with ceria, ceria-Cu, and ceria-Rh anode are shown to generate stable electric power with waste vegetable oil through direct oxidation of the fuel. While ceria only and ceria-Cu fuel cells generated electric power of 0.06 and 0.1 W cm^{-2}, respectively, ceria-Rh elevated the electric power to 0.25 W cm^{-2}. The performance of the ceria-Rh fuel cell was stable over 100 h for the waste vegetable oil without dilution. The only pre-treatment to the fuel was a filtration to remove particulates, making this fuel a more favorable choice than previously studied hydrocarbon fuels including jet fuels and Pennsylvania crude oil. The economical implication of this study is significant.

Acknowledgment

References

[1] E.P. Murry, T. Tsai, S.A. Barnett, Nature 400 (1999) 649–651.
[2] J. Liu, S.A. Barnett, Solid State Ionics 158 (2003) 11–16.
[3] S. Park, R.J. Gorte, J.M. Vohs, Appl. Catal. A: Gen. 200 (2000) 55–61.
[4] S. Park, J.M. Vohs, R.J. Gorte, Nature 404 (2000) 265–267.
[5] R.J. Gorte, H. Kim, J.M. Vohs, J. Power Sources 106 (2002) 10–15.
[6] R.J. Gorte, S. Park, J.M. Vohs, C. Wang, Adv. Mater. 12 (2000) 1465–1469.
[7] S. Park, R. Cracium, J.M. Vohs, R.J. Gorte, J. Electrochem. Soc. 146 (1999) 3603–3605.
[8] H. Kim, S. Park, J.M. Vohs, R.J. Gorte, J. Electrochem. Soc. 148 (2001) A693–A695.
[9] H. Kim, J.M. Vohs, R.J. Gorte, Chem. Commun. 22 (2001) 2334–2335.
[10] Z.F. Zhou, C. Gallo, M.B. Pague, H. Schobert, S.N. Lvov, J. Power Sources 133 (2004) 181–187.
[11] S. McIntosh, J.M. Vohs, R.J. Gorte, Electrochem. Solid-State Lett. 6 (2003) A240–A243.
[12] A. Atkinson, S. Barnett, R.J. Gorte, J.T.S. Irvine, A.J. McEvoy, M. Mogensen, S.C. Singhal, J. Vohs, Nat. Mater. 3 (2004) 17–27.
[13] J.M. Challinor, J. Anal. Appl. Pyrolysis 61 (2001) 3–34.
[14] T. Takeguchi, R. Kikuchi, T. Yano, K. Eguchi, K. Murata, Catal. Today 84 (2003) 217–222.
[15] S. McIntosh, J.M. Vohs, R.J. Gorte, J. Electrochem. Soc. 150 (2003) A470–A476.
[16] O. Costa-Nunes, J.M. Vohs, R.J. Gorte, J. Electrochem. Soc. 150 (2003) A858–A863.
[17] K. Kendall, C.M. Finnerty, G. Saunders, J.T. Chung, J. Power Sources 106 (2002) 323–327.
[18] Z.F. Zhou, R. Kumar, L.R. Rudnick, H. Schobert, S.N. Lvov, submitted for publication.
[19] A.J. Dijkstra, Eur. J. Lipid Sci. Technol. 104 (2002) 29–35.
[20] H. He, J.M. Vohs, R.J. Gorte, J. Power Sources 144 (2005) 135–140.