JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 947–954

Current efficiency for soybean oil hydrogenation in a solid polymer electrolyte reactor

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Received 14 October 1997; revised 27 January 1998

Soybean oil has been hydrogenated electrocatalytically in a solid polymer electrolyte (SPE) reactor, similar to that in H_2/O_2 fuel cells, with water as the anode feed and source of hydrogen. The key component of the reactor was a membrane electrode assembly (MEA), composed of a precious metal-black cathode, a RuO_2 powder anode, and a Nafion® 117 cation-exchange membrane. The SPE reactor was operated in a batch recycle mode at 60 °C and one atmosphere pressure using a commercial-grade soybean oil as the cathode feed. Various factors that might affect the oil hydrogenation current efficiency were investigated, including the type of cathode catalyst, catalyst loading, the cathode catalyst binder loading, current density, and reactant flow rate. The current efficiency ordering of different cathode catalysts was found to be Pd > Pt > Rh > Ru > Ir. Oil hydrogenation current efficiencies with a Pd-black cathode decreased with increasing current density and ranged from about 70% at $0.050\,\mathrm{A\,cm^{-2}}$ to 25% at $0.490\,\mathrm{A\,cm^{-2}}$. Current pulsing for frequencies in the range of 0.25–60 Hz had no effect on current efficiencies. The optimum cathode catalyst loading for both Pd and Pt was $2.0\,\mathrm{mg\,cm^{-2}}$. Soybean oil hydrogenation current efficiencies were unaffected by Nafion® and PTFE cathode catalyst binders, as long as the total binder content was ≤ 30 wt % (based on the dry catalyst weight). When the oil feed flow rate was increased from 80 to $300\,\mathrm{ml\,min^{-1}}$, the oil hydrogenation current efficiency at $0.100\,\mathrm{A\,cm^{-2}}$ increased from 60% to 70%. A high (70%) current efficiency was achieved at $80\,\mathrm{ml\,min^{-1}}$ by inserting a nickel screen turbulence promoter into the oil stream.

Keywords: *soybean oil hydrogenation*, *SPE reactor*, *membrane-electrode assembly*, *hydrogenation current efficiency*, *Pt-black*, *Pd-black*

1. Introduction

The partial hydrogenation of the unsaturated fatty acids in edible oil triglycerides is carried out to produce a more oxidatively stable product and/or change a normally liquid oil into a semi-solid or solid fat with melting characteristics designed for a particular application. Batch reactors, operating at 150–225 °C and 10–60 psig, are used commonly in commercial chemical catalytic oil hydrogenation plants, with Raney nickel or supported nickel catalysts [1]. The goal of a soybean oil partial hydrogenation process is to reduce the level of 18-carbon triene fatty acid (linolenic acid) with minimal synthesis of 18-carbon saturated fatty acid (stearic acid). High reaction temperatures, however, promote a number of deleterious side reactions, including the unfavourable production of *trans* fatty acid isomers (which are suspected of contributing to coronary heart disease by raising blood-levels of harmful high-density lipoprotein cholesterol and lowering protective high-density lipoprotein levels [2]) and the formation of cyclic aromatic fatty acids [3]. Precious metal powder catalysts (e.g., Pt and Pd) have been shown to lower the *trans* isomer levels during the partial hydrogenation of soybean oil, but their use has not been widespread due to difficulty in filtering the catalyst from the hydro-oil product.

Yusem, Pintauro, and coworkers [4] have shown that soybean oil can be hydrogenated electrochemically at a moderate temperature (70–75 °C) and one atmosphere pressure in an undivided Raney nickel powder flow-through packed bed reactor with a two-phase reaction medium of oil in a water/*t*-butanol solvent. Unfortunately, the reactor/reaction scheme suffered from a number of problems, including: (i) Contact of soybean oil with nonfood-grade *t*-butanol cosolvent and supporting electrolyte salt, (ii) a low operating current density (0.010–$0.020\,\mathrm{A\,cm^{-2}}$), and (iii) a high anode–cathode operating voltage. These complications have been circumvented in the present study by carrying out the oil hydrogenation reaction in a solid polymer electrolyte (SPE) reactor.

An SPE reactor for oil hydrogenation consists of anolyte and catholyte chambers separated by a thin, proton-conducting cation-exchange membrane. A porous anode and cathode are attached to each face of the membrane, forming a 'membrane-electrode-

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assembly' (MEA), similar to that employed in solid polymer electrolyte hydrogen/oxygen fuel cells [5]. Water, for example, is circulated past the back-side of the anode and is oxidized to O_2 gas and protons. Alternatively, humidified H_2 gas can be fed to the anode, in which case molecular hydrogen is oxidized to H^+. Electrogenerated protons migrate through the ion-exchange membrane under the influence of the applied electric field where they are reduced to atomic and molecular hydrogen. This hydrogen then reacts with the unsaturated fatty acids in an edible oil, where neat oil flows past the back-side of the cathode and permeates through the porous cathode structure. The principles of operation for an SPE reactor during edible oil hydrogenation are summarized in Fig. 1. The use of an SPE reactor eliminates the need for a supporting electrolyte and an organic cosolvent that can contaminate the hydro-oil product. The close proximity of the anode and cathode on a MEA and the high fixed-charge concentration of the hydrated solid polymer electrolyte membrane insures facile H^+ transport during current flow and a small anode–cathode voltage drop during reactor operation.

SPE reactors have been examined previously for organic electrochemical synthesis [6–11], including the electrocatalytic hydrogenation of cyclooctene, α-methyl styrene, diethyl maleate, and ethyl crotonate [6]. More recently, An *et al.* [12] have shown that edible oils (e.g., soybean and canola oils) and fatty acid mixtures can be hydrogenated electrochemically in an SPE reactor. Constant current electrolyses were carried out at a moderate temperature ($< 100\,°C$) and atmospheric pressure with water as the source of hydrogen and either Pd-black or Pt-black as the cathode material. An important finding of this work was the low *trans* fatty acid isomer content of electrochemically hydrogenated soybean oil products, which was in the range of 0–3.8% for a Pt cathode and 6.5–8.0% for a Pd cathode, as compared to 20–50% *trans* for a high-temperature chemical catalytic hydrogenation process using Raney nickel [1].

The work presented in this paper is an extension of the preliminary SPE reactor experiments described in [12]. Data presented below quantifies the effects of MEA design (catalyst type and loading and Nafion®/PTFE binder loading) and reactor operating conditions (e.g., oil flow rate and current density) on the current efficiency for soybean oil hydrogenation.

2. Experimental details

2.1. *SPE reactor*

Soybean oil was hydrogenated in a solid polymer electrolyte reactor, shown schematically in Fig. 2. The key component of the reactor was a membrane–electrode assembly (MEA), composed of catalytic anode and cathode powders that were hot-pressed as thin films onto the opposing surfaces of a Nafion® 117 cation-exchange membrane. The reactor was constructed of two stainless steel halves, that provided both mechanical support and electrical contact for the MEA. Neat soybean oil and deionized/distilled water (typically 10 g each) were back-fed separately to the cathode and anode, respectively, via grooved feed channels in the reactor housing. To eliminate metal corrosion, the anode feed channel was constructed of titanium. The MEA was secured tightly between the cathode and anode flow channels using silicon gaskets and stainless steel bolts. The

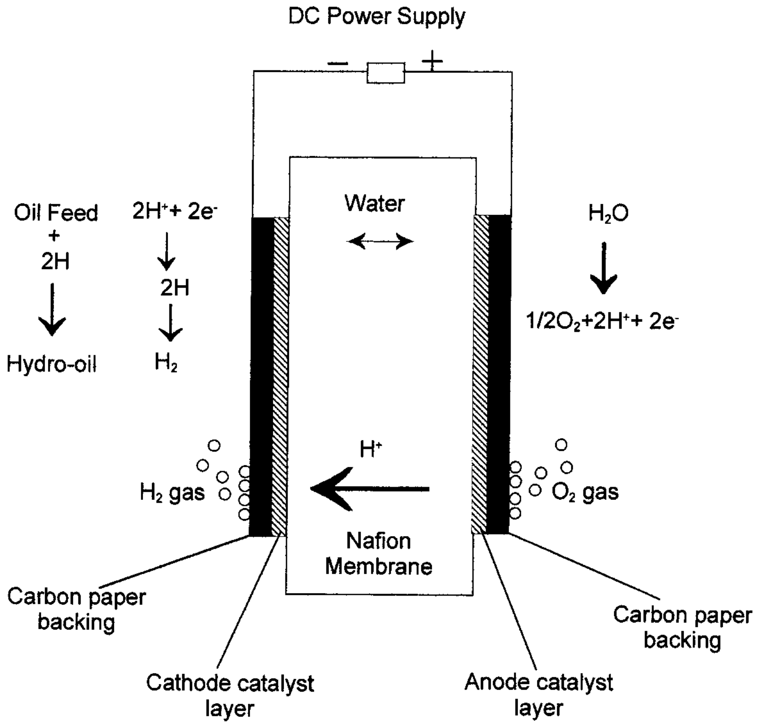

Fig. 1. Principles of operation of a SPE reactor during the electrohydrogenation of an edible oil.

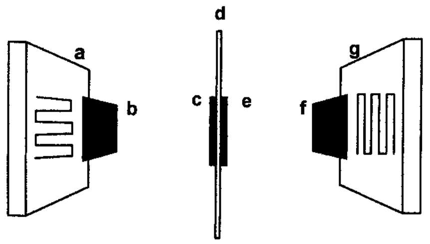

Fig. 2. Schematic diagram of the solid polymer electrolyte reactor. Key: (a) and (g) reactor blocks with cross-patterned flow field; (b) gas/oil permeable backing, cathode side; (c) cathode thin film catalyst layer; (d) Nafion® cation-exchange membrane; (e) anode thin film catalyst layer; (f) gas/water permeable backing, anode side.

SPE reactor was operated in a batch recycle mode by insertion into a circulation loop consisting of anolyte and catholyte peristaltic pumps and holding tanks immersed in a constant-temperature bath. All electrolyses were carried out at 60 °C, using refined and bleached soybean oil, provided by Ventura Foods, LLC, LouAna Division, Opelousas, LA.

2.2. *Membrane–electrode assembly fabrication*

MEAs with an apparent electrode area of 2 cm × 2 cm were prepared by a hot pressing method. For all experiments, Nafion® 117 was used as the SPE material and the anode was RuO_2 powder (Aldrich Chemical Co., Milwaukee, WI) at a loading of 2.5 mg cm^{-2}, with a 15 wt % PTFE/20 wt % Nafion® binder (the binder was prepared from Teflon-30 and a 5 wt % Nafion® emulsion that were purchased from ElectroChem, Inc., Woburn, MA). Cathodes were fabricated from precious metal-black powders (Pt, Pd, Rh, Ru and Ir, from Aldrich Chemical Co.) that were mixed with a known weight of Nafion® and PTFE. Anode and cathode powder/binder mixtures were coated on Toray carbon paper current collectors. After drying, the carbon paper electrodes were hot pressed (for 90 s at 250 °F and 160 atms) to the opposing surfaces of a Nafion® sheet.

2.3. *Oil analysis and the determination of current efficiency*

The chemical characterization of the starting soybean oil and hydrogenated products was performed in accordance with American Oil Chemists' Society (AOCS) procedures, as listed in 'Official Methods and Recommended Practices of the American Oil Chemists' Society' [13]. The fatty acid profile of initial and hydrogenated soybean oil samples was determined by gas chromatographic analysis of fatty acid methyl esters, (Perkin–Elmer Sigma 115 gas chromatograph with a flame ionization detector and a 6 foot glass-walled packed column containing 3% SP–2310 and 2% SP–2300 on 100/120 Chromosorb WAW from Supelco, Inc. Bellefonte, PA). The GC was operated isothermally at 200 °C with injector and detector temperatures of 250 °C and nitrogen as a carrier gas (at a flow rate of 20 $cm^3\,min^{-1}$). Confirmation of fatty acid peaks was achieved by comparison with the retention times of authentic samples available commercially.

The percentage current efficiency (CE) was calculated from the change in the unsaturated fatty acid composition of the initial and partially hydrogenated soybean oil according to the following equation:

$$CE = \frac{F \times M\left[\left(\frac{\Delta_{18:1}\times 2}{MW_{18:1}}\right) + \left(\frac{\Delta_{18:2}\times 4}{MW_{18:2}}\right) + \left(\frac{\Delta_{18:3}\times 6}{MW_{18:3}}\right)\right]}{\text{Total charge passed}} \times 100 \tag{1}$$

where $\Delta_{18:1}$, $\Delta_{18:2}$ and $\Delta_{18:3}$ are the change in the weight percent concentrations of oleic, linoleic and linolenic acids before and after an electrolysis, as obtained from GC analyses. The factors 2, 4 and 6 are the electrical equivalents for oleic, linoleic, and linolenic acids, respectively, M is the total mass of soybean oil utilized in an experiment, MW is the molecular weight of each fatty acid ($MW_{18:1}$ is 282.465 g mol^{-1}, $MW_{18:2}$ is 280.450 g mol^{-1} and $MW_{18:3}$ is 278.435 g mol^{-1}) and F is Faraday's constant.

The overall degree of oil hydrogenation is usually quantified by the iodine value (IV), which is expressed in terms of the number of centigrams of iodine absorbed per gram of oil (I_2 reacts with the double bonds of unsaturated fatty acids). In the present study, the iodine value of oil samples was determined directly from the GC fatty acid composition (AOCS Method Cd 1c-85 [13]).

3. Results and discussion

3.1. *Performance of different cathode catalysts*

Five precious metal powder catalysts were examined for soybean oil hydrogenation in the SPE reactor, Pd-black, Pt-black, Rh-black, Ru-black and Ir-black. In these electrolyses, the cathode catalyst loading was fixed at 2 mg cm^{-2}, with a mixture of 10 wt % PTFE and 10 wt % Nafion® as the binder (binder content was based on the dry catalyst weight). The oil flow rate was 80 ml min^{-1}, the temperature was 60 °C, the pressure was one atmosphere, and the applied constant current density was 0.100 A cm^{-2}. The chemical properties of the soybean oil products and the current efficiency performance of the SPE reactor for the different cathodes are listed in Table 1. A Pd-black catalyst exhibited the highest oil hydrogenation current efficiency, at nearly 60%. Pt-black also performed well (40% current efficiency), but the current efficiencies with the other three catalysts were very low (less than 30%). In all experiments, current losses were due solely to hydrogen gas evolution. Since the activity of the catalysts for oil hydrogenation will mirror directly the current efficiency ordering, the oil hydrogenation reactivity sequence in the SPE reactor was as follows:

$$\mathrm{Pd} > \mathrm{Pt} > \mathrm{Rh} > \mathrm{Ru} > \mathrm{Ir}$$

A similar activity ordering was observed during the chemical catalytic hydrogenation of soybean oil

Table 1. Performance of different precious metal catalysts during the electrocatalytic hydrogenation of soybean oil

Catalyst type	*Charge passed* /C g^{-1}	*Fatty acid profile*/wt%				*IV*	*Voltage drop* /V	CE /%
		C18:0	*C18:1*	*C18:2*	*C18:3*			
Starting oil		2.8	21.1	57.3	7.4	137	–	–
Pd-Black	628.9	25.6	30.7	29.7	2.9	85	1.6 ~ 1.7	58.5
Pt-Black	608.6	19.7	24.5	39.8	4.5	102	1.6 ~ 1.7	40.0
Rh-Black	620.8	11.5	28.1	44.7	4.5	113	1.6 ~ 1.7	28.4
Ru-Black	620.8	10.9	23.5	48.6	6.0	120	1.6 ~ 1.7	20.2
Ir-Black	620.8	8.3	23.5	50.9	6.2	125	1.6 ~ 1.7	14.8

Reaction temperature: 60 °C; current density: 0.100 A cm^{-2}; oil feed flow rate: 80 ml min^{-1}; catalyst loading: 2.0 mg cm^{-2}.

[14, 15]. The fatty acid selectivities of the noble metal cathodes were not nearly as high as those found during the electrocatalytic hydrogenation of soybean oil at a Raney nickel cathode [4] (i.e., higher concentrations of fully saturated stearic acid and triene fatty acid were observed with the noble metal cathodes). This observation is consistent with literature data for the high temperature chemical catalytic hydrogenation of soybean oil with Pt or Pd [16, 17].

Prior studies have shown that the hydrogenation activity of a catalyst composed of two or more precious metals can be higher than that for any one of the individual metals [18]. To determine if this were the case in an SPE reactor, oil hydrogenation experiments were carried out with cathodes containing a mixture of Pt-black and Pd-black (where the total catalyst loading was held constant at 2.0 mg cm^{-2}). The current efficiency results from these electrolyses, which are shown in Fig. 3, indicate no synergistic catalyst effect during the electrochemical hydrogenation process; the current efficiency decreased monotonically as the percentage of Pt in the Pt–Pd mixture was increased.

3.2. *Effect of binder loading*

In our initial SPE oil hydrogenation experiments [12] and in the electrolyses reported above, cathodes were fabricated using both PTFE and Nafion binders. Good electrical conductivity between catalyst particles, with no observable physical degradation of the cathode over the course of an electrolysis was achieved with a mixture of 10 wt % Nafion® and 10 wt % PTFE. In a new set of experiments, the PTFE loading was held constant at 10 wt % and the Nafion® content was varied (from 0 to 40 wt %) or the Nafion® content was maintained at 10 wt % and the amount of PTFE was changed (from 0 to 40 wt %). For all experiments, the oil flow rate was 80 ml min^{-1}, the current density was 0.100 A cm^{-2}, and the cathode catalyst was either Pt-black or Pd-black, at 2 mg cm^{-2}. As shown in Fig. 4, the current efficiency was constant for both Pt and Pd when the total binder content was $\leqslant$30 wt % (including Nafion®/no PTFE and PTFE/no Nafion®). A linear decrease in current efficiency with binder content was observed when the total binder exceeded 20 wt %, due presumably to blockage of cathode catalyst surface sites for H$^+$ reduction and/or oil hydrogenation. The high current efficiencies with high PTFE and low Nafion® contents were attributed to the hydrophobicity of PTFE that was drawing soybean oil reactant into the porous cathode structure of the MEA. When the binder was predominantly Nafion®, the current efficiency was also high due to an improvement in proton transport to more cathode catalyst particles (resulting in a lower local current density on the cathode catalyst). As a consequence of these results, subsequent MEAs were fabricated with a binder mixture of 10 wt % Nafion® and 10 wt % PTFE.

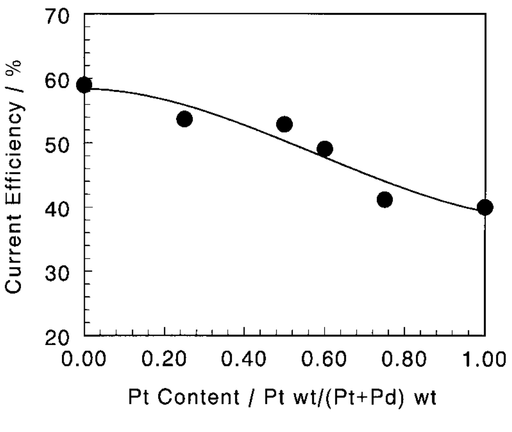

Fig. 3. Effect of Pd/Pt mixed catalyst composition on soybean oil hydrogenation current efficiency.

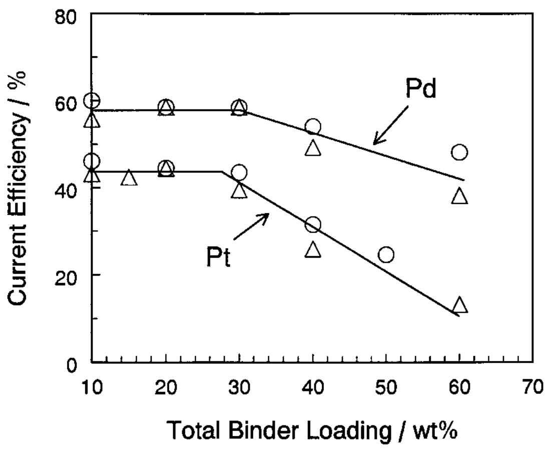

Fig. 4. Effect of Nafion®/Teflon binder composition and loading on soybean oil hydrogenation current efficiency. Key: (○) 10% Nafion® (fixed) with varying amount of PTFE; (△) 10% Teflon (fixed) with varying amounts of Nafion®.

3.3. *Effect of catalyst loading*

Studies on fuel cell MEAs have shown that an optimum catalyst loading exists, in terms of the cathode surface area and current density per unit weight of catalyst [5, 19]. In contrast to that in a fuel cell, the cathode in an SPE oil hydrogenation reactor serves two purposes; it is the conducting metal matrix on which protons are reduced electrochemically to atomic and molecular hydrogen and it also furnishes catalytic sites for the chemical reaction of hydrogen with oil. The dependence of oil hydrogenation current efficiency on catalyst loading for either a Pt or Pd cathode is shown in Fig. 5. A maximum current efficiency was found at a loading of approximately 2 mg cm^{-2}. At lower catalyst loadings, the local current density for proton reduction was high (lower cathode area), resulting in excessive hydrogen gas evolution. At high catalyst loadings, the porous cathode was too thick which restricted access of oil to interior portions of the cathode where hydrogen was electrogenerated.

3.4. *Applied current and cell voltage behaviour*

Normally, the current efficiency for an electrocatalytic hydrogenation reaction decreases with increasing current density [4, 20], due to an imbalance in the production and consumption rates of hydrogen. For the electrocatalytic hydrogenation of soybean oil in an SPE reactor with either a Pt-black or Pd-black cathode, a similar current density/current efficiency trend was observed, as shown in Fig. 6. Between 0.050 and 0.490 A cm^{-2} there was a steady decrease in current efficiency with current density. Between 0.250 and 0.490 A cm^{-2} the rate of change in current efficiency with current density was small, but the current efficiencies were low, especially for the Pt cathode. The anode/cathode voltage drop during SPE reactor operation is plotted against the apparent current density in Fig. 7. There was no detectable difference in operating voltage for a Pt or Pd cathode, with a modest increase in cell voltage (from 1.6 to 2.3 V) when the current density was increased from 0.050 to 0.490 A cm^{-2}.

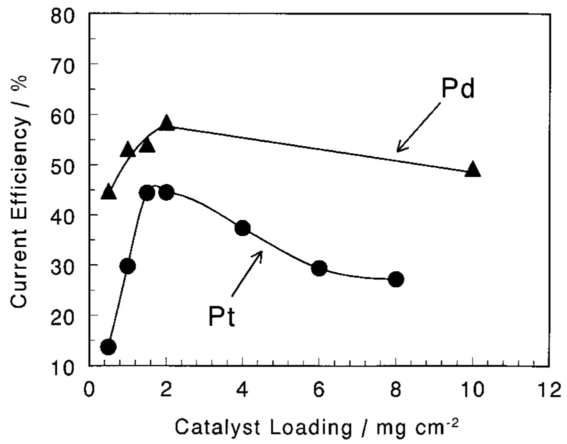

Fig. 5. Effect of cathode catalyst loading on soybean oil hydrogenation current efficiency for a constant applied current density of 0.100 A cm^{-2} and a temperature of 60 °C.

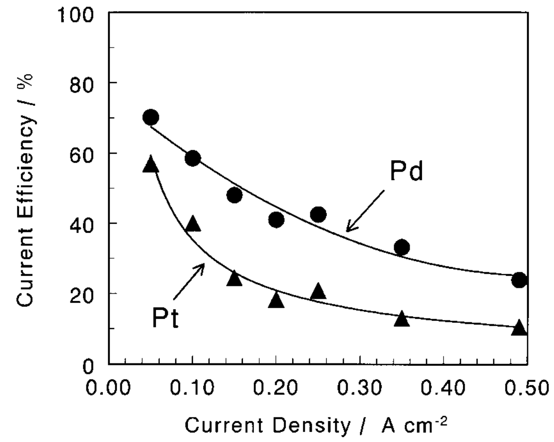

Fig. 6. Effect of applied current density on soybean oil hydrogenation current efficiency for a cathode catalyst loading of 2.0 mg cm^{-2} and a temperature of 60 °C.

For an electrochemical oil hydrogenation process, the size (and capital cost) of the reactors for a specified product output is determined by the net production rate of hydrogenated oil per unit geometric area of cathode, which is directly proportional to the product of the current efficiency and current density. The production rate (with units of kg m^{-2} h^{-1}) of an IV 90 soybean oil (i.e., an oil with 32% of its double bonds saturated) was calculated using the data in Fig. 6 and the following formula:

$$\text{Production rate} = i\left(\frac{CE}{100}\right)\left(\frac{1}{0.32 \times 1.054 \times 10^6}\ \text{kg/C}\right) \times \left(1 \times 10^4\,\text{cm}^2/\text{m}^2\right)(3600\,\text{s/h}) \quad (2)$$

where the current density i has units of A cm^{-2} and the constant 1.054×10^6 C is the charge required to fully saturate one kilogram of soybean oil. As shown in Fig. 8, the production rate of hydrogenated oil with a Pd cathode increased with increasing current density up to 0.350 A cm^{-2} and then stabilized at just under 13.0 kg m^{-2} h^{-1} (the decrease in current efficiency with current density was offset by the higher

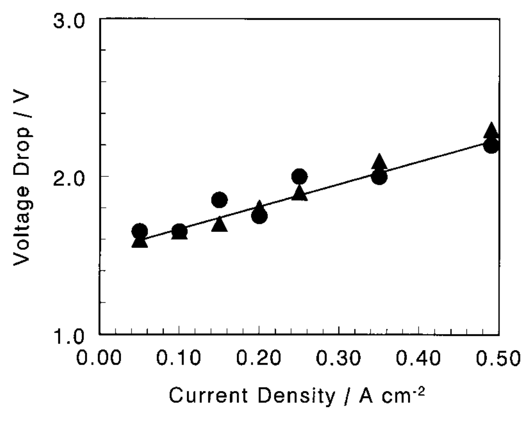

Fig. 7. Anode/cathode voltage drop during soybean oil hydrogenation in the SPE reactor.

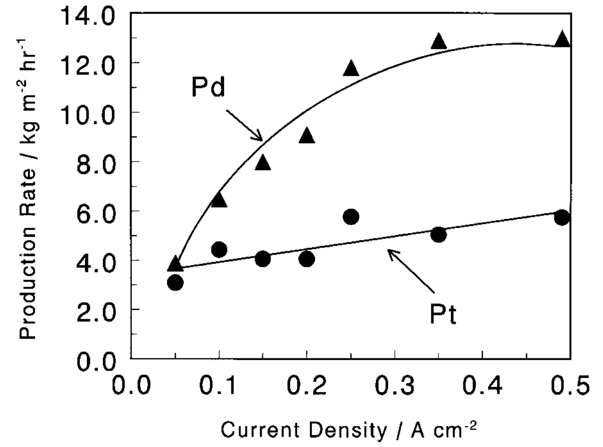

Fig. 8. Production rate of a partially hydrogenated soybean oil (IV 90) as a function of applied current density in the SPE reactor.

current density, so that the product of the two increased). The production rate with a Pt cathode was much lower than that with Pd, due to the lower hydrogenation current efficiencies, with a modest and linear increase in production rate from 0.050 to 0.490 A cm^{-2}. Based on the Pd-black data, there will be a fourfold decrease in the size (and cost) of the SPE reactors when the operating current density is increased from 0.050 to 0.350 A cm^{-2} (assuming the cost of the reactors scales linearly with the geometric cathode area). The SPE reactor power consumption (with units of kW h kg^{-1}) for the synthesis of an IV 90 hydrogenated soybean oil was determined using the data in Figs. 6 and 7 and the following formula:

$$\text{Power consumption} = \frac{iV(2.78\times10^{-7}\,\text{kW h/J})(1\times10^{4}\,\text{cm}^2/\text{m}^2)(3600\,\text{s/h})}{\text{Production rate}} \qquad (3)$$

where V is the cell voltage (V). The reactor power consumption for a Pt-black or Pd-black cathode are plotted vs the applied current density in Fig. 9. As would be expected, the reactor power requirement increased with increasing current density, but the rate of increase was much smaller than the product of i and V (i.e., the power increased by only a factor of about four for a Pd cathode when the current density increased from 0.050 to 0.350 A cm^{-2}) because higher oil production rates were achieved at the higher current densities. For the SPE oil hydrogenation reactor, it is expected that reactor costs will dominate over operating costs, hence a high operating current density would be preferable (this would be especially true if the anode reaction were the oxidation of H_2 to H^+, since the operating cell voltage would be reduced by at least 1.23 V and the power consumption would be lowered from that in Fig. 9 by a factor of about four).

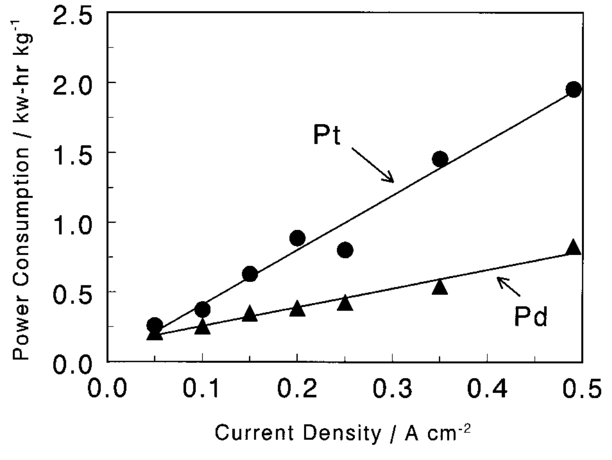

Fig. 9. Variation in power consumption in the SPE reactor per kg of oil product with applied current density during the production of a partially hydrogenated (IV 90) soybean oil.

Pulsing the applied current has been shown, both experimentally and theoretically, to improve the current efficiency and/or selectivity of electroorganic reactions [21, 22]. In the present study, soybean oil hydrogenation experiments were carried out using high current/low current pulsed square wave currents (with current densities of 0.188/0.013, 0.175/0.025 and 0.150/0.050 A cm^{-2}) and a 50% duty cycle. For all electrolyses, the time-averaged current density was equal to 0.100 A cm^{-2} so that a direct comparison could be made with the data in Fig. 6. The resulting soybean oil hydrogenation current efficiencies for Pt-black and Pd-black cathodes are plotted in Figure 10 as a function of frequency (which was varied from 0.25 to 60 Hz). As compared to the constant current case, no change in oil hydrogenation current efficiency was observed with current pulsing. Obviously, the time constant for the rate limiting step during soybean oil hydrogenation was slow as compared to the pulsing rate (i.e., the characteristic time was much greater than 4 s, because the current efficiency at 0.25 Hz was identical to that for a constant current). Since the reaction rate of oil and hydrogen on a precious metal catalyst is known to be reasonably fast at 60 °C [14], we have concluded that the rate limiting step is the delivery of soybean oil reactant to catalyst sites in the MEA. It should be noted that the results

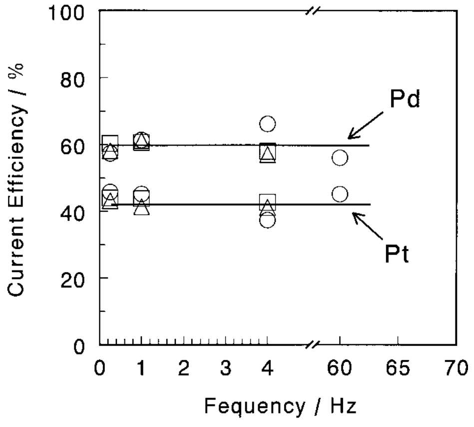

Fig. 10. Effect of pulsed current frequency on the current efficiency for soybean oil hydrogenation. Pulsed current duty cycle: 50%. Key: (△) ON/ON pulsed current densities of 0.150 A cm^{-2}/0.050 A cm^{-2}; (□) ON/ON pulsed current densities of 0.175 A cm^{-2}/0.025 A cm^{-2}; (○) ON/ON pulsed current densities of 0.188 A cm^{-2}/0.013 A cm^{-2}.

in Fig. 10 indicate that the SPE reactor can be operated using a half-wave rectified 60 cycle AC current with no adverse effect on current efficiency (such a current mode would eliminate the need for rectifiers and may lower the capital costs of a oil hydrogenation plant).

3.5. *Flow rate effects*

Triglyceride molecule access to the catalyst surface is essential for the efficient utilization of electrogenerated hydrogen in an SPE reactor. It is reasonable to assume that essentially all of the soybean oil was hydrogenated in a thin catalyst layer adjacent to the carbon paper current collector. The primary resistance to oil mass transfer from the feed channel to the catalyst was, therefore, the porous carbon paper, although there also may have been a stagnant oil boundary layer on the feed channel side of the paper. To determine whether oil mass transfer was affecting hydrogenation current efficiencies, electrolyses were performed at oil flow rates varying from 80 to 400 ml min^{-1}, with and without a nickel mesh turbulence promoter (the nickel mesh was shown in blank tests to have no catalytic activity). In these experiments, the water flow rate past the anode was held constant at 80 ml min^{-1}. From the width (0.28 cm) and depth (0.17 cm) of the serpentine, grooved feed channel, the range of oil flow rates translated into linear velocities of 28–141 cm s^{-1} or Reynolds numbers of 33–165. For these experiments, the current density was 0.100 A cm^{-2} and the MEA cathode was composed of either Pd-black or Pt-black (at 2.0 mg cm^{-2}).

As shown in Figure 11, oil flow rate effects were more pronounced with a Pd cathode, due to its higher oil hydrogenation activity. With no turbulence promoter, the current efficiency increased with flow rate up to 300 ml min^{-1}, as boundary-layer resistance in the flowing oil was eliminated. At a flow rate of 400 ml min^{-1} there was a pronounced decrease in current efficiency which was attributed to water leakage into the oil feed channel. At the high oil flow rate, a pressure drop was generated across the MEA (with a lower pressure on the oil side due to its higher linear velocity) which produced a small but observable convective water flux. As water was transported into the oil feed channel, it filled a portion of the void volume in the carbon paper and decreased oil access to the catalyst layer beneath the paper. When a turbulence promoter was utilized with a Pd catalyst cathode, the oil hydrogenation current efficiencies were essentially constant from 80 to 300 ml min^{-1}, with a drop-off in current efficiency at 400 ml min^{-1}. The maximum current efficiency for soybean oil hydrogenation at 0.100 A cm^{-2} with a Pd-black catalyst was found to be approximately 70%, at 300 ml min^{-1} with no turbulence promoter or at a flow rate as low as 80 ml min^{-1} with a turbulence promoter. When the cathode catalyst was Pt, oil hydrogenation current efficiencies were essentially independent of oil flow rate and unchanged in the presence and absence of a turbulence promoter, due to the sluggish reaction of oil with electrogenerated hydrogen.

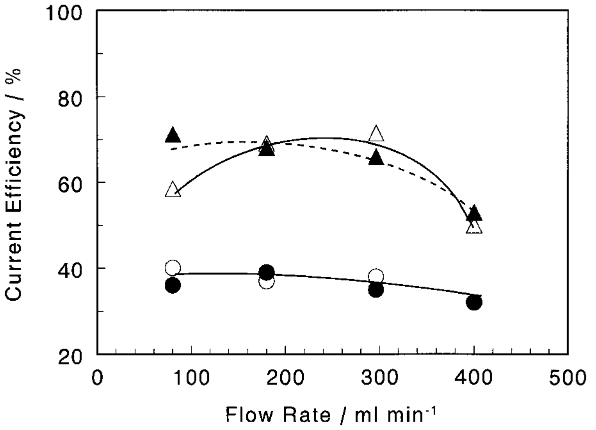

Fig. 11. Effect of oil feed flow rate on the current efficiency for soybean oil hydrogenation. Key: (▲) and (△) Pd-black catalyst cathode; (●) and (○) Pt-black catalyst cathode. Closed symbols: data collected with a nickel mesh turbulence promoter in the oil stream; open symbols: no turbulence promoter.

4. Conclusions

Soybean oil has been hydrogenated electrocatalytically in a solid polymer electrolyte (SPE) reactor, similar to that used in H_2/O_2 fuel cells, with water as the anode feed and source of hydrogen. The key component of the reactor was a membrane–electrode assembly (MEA), composed of a precious metal-black cathode, a RuO_2 powder anode, and a Nafion® 117 cation-exchange membrane. The anode and cathode catalyst powders were mixed with Nafion® and PTFE binders, coated on carbon paper current collectors, and then hot-pressed to the opposing surfaces of the Nafion® membrane. The SPE reactor was operated in a batch recycle mode at 60 °C and one atmosphere pressure, with a commercial-grade soybean oil as the cathode feed.

Various factors that might affect the oil hydrogenation current efficiency were investigated, including the type of cathode catalyst, catalyst loading, the cathode catalyst binder loading, current density, and reactant flow rate. The current efficiency ordering for different cathode catalysts was Pd > Pt > Rh > Ru > Ir, which mirrored the catalyst activity sequence for oil hydrogenation in a higher temperature/elevated pressure chemical catalytic process. At a reaction temperature of 60 °C and an oil flow rate of 80 ml min^{-1}, oil hydrogenation current efficiencies decreased with increasing current density and ranged from about 70% at 0.050 A cm^{-2} to 25% at 0.490 A cm^{-2} for a Pd-black cathode. The production rate (i.e., the product of the current density and current efficiency) of a partially hydrogenated, IV 90 soybean oil, increased up to 0.350 A cm^{-2} because the decrease in current efficiency was offset by the higher current density. High current/low current pulsing, with a frequency in the range of 0.25–60 Hz had no affect on oil hydrogenation current efficiencies, presumably because mass transfer of oil to cathode reaction sites was controlling the hydrogenation rate.

The optimum cathode catalyst loading for both Pd and Pt was 2.0 mg cm^{-2}. Soybean oil hydrogenation current efficiencies were unaffected by Nafion® and Teflon cathode catalyst binders, as long as the total binder content was $\leqslant 30$ wt % (based on the dry catalyst weight). When the oil feed flow rate was increased from 80 to 300 ml min^{-1}, the oil hydrogenation current efficiency with a Pd-black cathode increased from 60 to 70%. A high (70%) current efficiency could achieved with Pd at a low flow rate (80 ml min^{-1}) by inserting a nickel screen turbulence promoter into the oil feed stream. Current efficiencies with a Pt-black cathode were found to be independent of the flow rate, due presumably to the slow reaction of oil and hydrogen on the catalyst surface.

Acknowledgements

This work was supported by the Cooperative State Research Service, US Department of Agriculture, under Agreement No. 94-37500-0634. The authors thank Ventura Foods LLC, Lou Ana Division for providing soybean oil used in this study.

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