The Electrochemical Hydrogenation of Edible Oils in a Solid Polymer Electrolyte Reactor. II. Hydrogenation Selectivity Studies

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ABSTRACT: Soybean oil has been hydrogenated electrochemically in a solid polymer electrolyte (SPE) reactor at 60°C and 1 atm pressure. These experiments focused on identifying cathode designs and reactor operation conditions that improved fatty acid hydrogenation selectivities. Increasing oil mass transfer into and out of the Pd-black cathode catalyst layer (by increasing the porosity of the cathode carbon paper/cloth backing material, increasing the oil feed flow rate, and inserting a turbulence promoter into the oil feed flow channel) decreased the concentrations of stearic acid and linolenic acid in oil products [for example, an iodine value (IV) 98 oil contained 12.2% $C_{18:0}$ and 2.3% $C_{18:3}$]. When a second metal (Ni, Cd, Zn, Pb, Cr, Fe, Ag, Cu, or Co) was electrodeposited on a Pd-black powder cathode, substantial increases in the linolenate, linoleate, and oleate selectivities were observed. For example, a Pd/Co cathode was used to synthesize an IV 113 soybean oil with 5.3% stearic acid and 2.3% linolenic acid. The *trans* isomer content of soybean oil products was in the range of 6–9.5% (corresponding to specific isomerization indices of 0.15–0.40, depending on the product IV) and did not increase significantly for high fatty acid hydrogenation selectivity conditions.

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We have reported recently on a new, low temperature and atmospheric pressure electrochemical technique for partially hydrogenating edible oils and fatty acid mixtures (1,2; Warner, K., W.E. Neff, and P. Pintauro, unpublished data). The method employed a solid polymer electrolyte (SPE) reactor, similar to that used in H_2/O_2 fuel cells, with water as the source of hydrogen. The key component of the reactor was a "Membrane-Electrode-Assembly" (MEA), composed of RuO_2 powder (for the anode) and either Pt-black or Pd-black powder (for the cathode) that were hot-pressed as thin (fixed-bed) films onto the opposing surfaces of a Nafion cation-exchange membrane (E.I. DuPont deNemours, Inc.,

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Wilmington, DE). During reactor operation at a constant applied current, water was back-fed to the RuO_2 anode where it was oxidized electrochemically to O_2 and H^+. Protons migrated through the Nafion membrane under the influence of the applied electric field and contacted the Pt or Pd cathode where they were reduced to atomic and molecular hydrogen. The oil or fatty acid mixture was circulated past the back side of the cathode and double bonds reacted with the electrogenerated hydrogen species. A schematic diagram of the structure and reactions at an MEA during oil hydrogenation is shown in Figure 1.

In our first paper (1), preliminary data were presented on SPE reactor operation during the hydrogenation of soybean, canola, and cottonseed oils and mixtures of fatty acid and fatty acid methyl esters. The reactor operated at a temperature between 60 and 80°C, with an applied current density of 0.10 A/cm². Reaction products, with an iodine value (IV) in the range of 60–105, were characterized by a higher stearic acid content and a lower percentage of *trans* fatty acid isomers, as compared to a traditional chemical catalytic hydrogenation scheme with a nickel catalyst. For example, the $C_{18:0}$ content of soybean oil hydrogenated at a Pt-black cathode was in the range of 20–33% for oil products with an IV between 102 and 80, whereas the stearic acid content with a Pd-black cathode was 20–28% for the same IV range. The total *trans* isomer content of soybean oil products with a Pt-black cathode, on the other hand, was lower than that with Pd (<4% *trans* with a Pt cathode vs. 6.5–10% *trans* for a Pd cathode).

In a second paper (2) we focused our attention on the electrical efficiency of hydrogen addition to the unsaturated fatty acids in soybean oil (i.e., the so-called electrochemical current efficiency for oil hydrogenation), using Pt or Pd catalyst cathodes. The effects of current density, oil flow rate, type of cathode catalyst, and variations in MEA fabrication/composition on the hydrogenation current efficiency were determined. Such data are important for the economic evaluation of the SPE reactor process, since the size and number of SPE reactors in a commercial-size plant will depend on the product of the operating current density and hydrogenation current efficiency. In all experiments a Pd-black cathode worked significantly better than Pt in terms of the utilization of electrogenerated hydrogen. From bench-scale experiments the maximum production rate
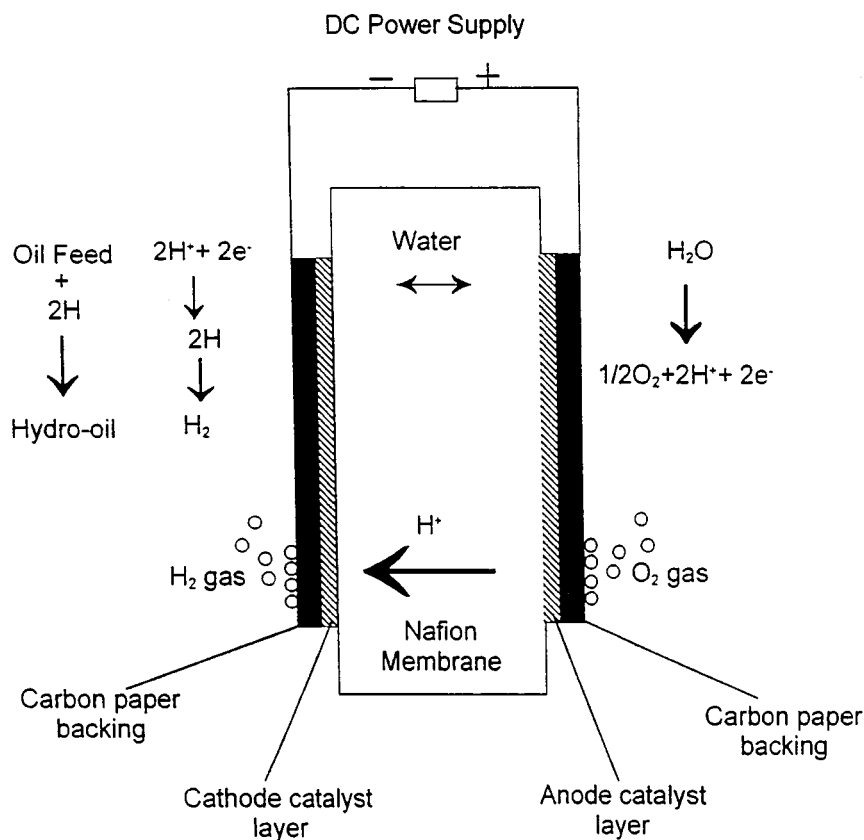
DC Power Supply

FIG. 1. Principles of operation of a solid polymer electrolyte reactor during the electrochemical hydrogenation of an oil.

for an IV 90 soybean oil with a Pd-black cathode at 60°C and atmospheric pressure was found to be 13 kg/h m^2 of geometric electrode area (an apparent operating current density of 0.350 A/cm^2 and an anode/cathode voltage drop of 1.8 V). At this production rate and cell voltage the reactor's electrical power requirement was 0.75 kw-h per kg of product. Most of the power was consumed in the reactor by the anodic water oxidation reaction. If H$_2$ gas were fed to the anode (where it would be electrochemically oxidized to H$^+$), the reactor's power consumption would decrease to about 0.1 kw-h/kg.

The composition and heated oil characteristics of soybean oils hydrogenated electrochemically were also examined (Warner, K., W.E. Neff, and P. Pintauro, unpublished results). IV 90 and 104 oil samples from the SPE reactor showed very low levels of peroxides and free fatty acids. Sensory analysis of the odor of hydrogenated oils heated to 190°C showed significantly less intensity of heated oil odors and hydrogenated odor in the SPE reactor products than in commercially (catalytically) hydrogenated oils. Electrochemical hydrogenation produced deodorized oils with lower levels of *trans* fatty acid and lower intensity levels of off-odors than did commercial hydrogenation.

The present paper deals with recent work on improving the fatty acid hydrogenation selectivities in an SPE reactor with a Pd-black cathode and soybean oil feed. Variations in cathode design and reactor operating conditions were examined. Our goal was to synthesize a partially hydrogenated soybean oil

with a linolenic acid concentration of ≤3% [the value of 3% is a generally recognized benchmark specification for a partially hydrogenated soybean oil (3,4)], a low concentration of *trans* fatty acid isomers, and a stearic acid content lower than that found in our previous studies.

EXPERIMENTAL PROCEDURES

MEA fabrication. MEA with an apparent cathode area of 4 cm^2 (dimensions of 2 × 2 cm), were prepared by: (i) mixing Pd-black catalyst powder with poly(tetrafluoroethylene) (PTFE) and Nafion binders in an isopropyl alcohol solution (cathode) or RuO$_2$ powder with PTFE/Nafion/isopropyl alcohol (anode), (ii) coating carbon paper or carbon cloth sheets with the catalyst/binder solution, (iii) evaporating the alcohol, and (iv) hot-pressing the sheets to the opposing surfaces of a Nafion 117 cation exchange membrane at 160 atm and 250°F for 90 s (with the anode and cathode catalyst layers facing the membrane) (1). Catalyst loadings were 2.5 mg/cm^2 for the anode and between 0.25 and 10.0 mg/cm^2 for the cathode.

Oil hydrogenation experiments. Hydrogenation experiments were carried out with an SPE reactor operating in a batch recycle mode [see Figs. 2 and 3 (1) for details of the reactor design and batch recycle apparatus]. In all experiments neat refined and bleached (RB) soybean oil (Lou Ana Foods division, Ventura Food, LLC, Opelousas, LA) was fed to the cathode and deionized and distilled water was circulated past

the anode (oil and water flowed through serpentine, grooved channels in the reactor housing). The starting oil and hydrogenated products were analyzed for fatty acid composition, IV, and total *trans* isomers using standard AOCS methods (1). Three batches of RB soybean oil were utilized in the experiments. The fatty acid composition of the oil feeds differed somewhat, with 2.8–4.0% stearic acid, 21.1–24.7% oleic acid, 53.8–57.3% linoleic acid, 6.1–7.7% linolenic acid, and an IV of 130–137. Linolenate, linoleate, and oleate hydrogenation selectivities (denoted as SLn, SLo, and SO, respectively) were computed from the rate constants for the sequential hydrogenation of triene, diene, and monoene fatty acids, as determined from the initial and final fatty acid profiles of soybean oil samples and from first-order rate expressions for fatty acid hydrogenation (1). The current efficiency for oil hydrogenation (1), a quantitative measure of the efficiency of electrogenerated hydrogen addition to a double bond, was calculated from: (i) the change in the soybean oil's fatty acid composition at the conclusion of an experiment (which is directly proportional to the number of hydrogen atoms that actually combine with the oil) and (ii) the total number of H atoms generated electrochemically on the Pd-black cathode catalyst, which is equal to the total electrical charge passed in an oil experiment (the charge is equal to the product of the constant applied current density, with units of A/cm^2, the geometric electrode area, 4 cm^2, and the total time of an experiment). We have found previously (1,2) that current efficiency losses during oil/fatty acid hydrogenation were due solely to H_2 gas evolution.

RESULTS AND DISCUSSION

Effect of hydrogen supply. In a batch chemical catalytic oil hydrogenation process, high temperature and pressure conditions (typically 150–225°C and 10–60 psig) are used to maintain a sufficiently high concentration of hydrogen on the catalyst surface (5). For the sequential hydrogenation of triene, diene, and monoene fatty acids in soybean oil, Coenen (6) found that those operating conditions which lowered the hydrogen concentration on the catalyst surface (e.g., pressure and slurry reactor agitation rate) increased both the fatty acid

hydrogenation selectivity and the degree of *cis*-to-*trans* fatty acid isomerization. In an electrochemical hydrogenation scheme, atomic and molecular hydrogen are generated *in-situ* directly on the catalyst surface by the reduction of protons. Thus, the hydrogen supply to the catalyst is controlled by varying the operating current density in the SPE reactor.

The effect of current density on fatty acid hydrogenation selectivity in the SPE reactor with a Pd-black cathode is shown in Table 1. In these experiments, Toray carbon paper (0.17 mm in thickness; Toray Industries, Tokyo, Japan; available from E-TEK, Inc., Natick, MA) was used as the backing material (current collector) for both the anode and cathode, and the cathode catalyst loading was fixed at 2.0 mg/cm^2. The temperature, pressure, and oil flow rate were 60°C, 1.0 atm, and 80 mL/min, respectively. The total electrical charge passed through the catalyst cathode was approximately the same for each experiment and the product IV was allowed to vary from one experiment to another, depending on the current efficiency of the electrohydrogenation reaction. The results in Table 1 show that the hydrogenation current efficiency and, thus, the overall extent of oil hydrogenation decreased with increasing current density. From the calculated values of SLn, SLo, and SO, it is apparent that variations in current density had essentially no effect on the hydrogenation selectivities. Also, the specific *trans* isomerization selectivity [denoted as SI and defined as the percentage increase in *trans* fatty acid content per unit change in the oil's IV (7)] did not correlate with the applied current density. We have concluded from these experiments that the electrochemical hydrogen generation rate is not a key parameter affecting oil hydrogenation selectivity in an SPE reactor.

Oil mass transfer effects. A series of oil hydrogenation experiments was performed to assess the role of oil mass transfer into and out of the MEA's cathode structure on oil hydrogenation selectivity. Oil mass transfer was varied by: (i) increasing the feed flow rate and/or generating a turbulent flow pattern of oil passing over the back side of the MEA, to reduce oil boundary-layer effects on the carbon paper cathode current collector; (ii) changing the Pd catalyst layer thickness beneath the carbon paper; and (iii) examining carbon papers of differing porosity and thickness.

TABLE 1
Effect of Current Density on Soybean Oil Hydrogenation Selectivity and *cis/trans* Isomerization for Pd Catalyst[a]

Current density (A/cm²)	Fatty acid profile					Current efficiency				
	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	IV	(%)	SLn	SLo	SO	SI[b]
0.05	24.1	32.5	29.7	2.9	87	70	1.35	1.08	1.46	0.19
0.10	25.6	30.7	29.7	2.9	85	59	1.35	0.96	1.30	0.16
0.15	17.4	35.3	32.7	3.2	95	48	1.43	1.38	1.97	0.24
0.20	16.1	33.0	35.9	4.0	101	41	1.31	1.22	1.59	0.18
0.25	17.2	32.4	35.2	4.2	100	43	1.17	1.14	1.34	0.15
0.35	12.7	30.3	41.1	4.7	110	33	1.17	1.06	1.24	0.14
0.49	11.3	31.3	41.4	4.7	111	24	1.19	1.22	1.46	0.15

[a]Cathode: 2.0 mg/cm² Pd-black, 10% Nafion (E.I. DuPont de Nemours, Inc., Wilmington, DE), 10% poly(tetrafluoroethylene) (PTFE), Toray carbon paper backing (0.17 mm thickness; Toray Industries, Tokyo, Japan; available from E-TEK, Inc., Natick, MA); temperature: 60°C; pressure: 1.0 atm; flow rate: 80 mL/min.
[b]Specific isomerization index = % increase in *trans* isomers/change in oil iodine value (IV); SLn, linolenate selectivity; SLo, linoleate selectivity; SO, oleate selectivity.

The effect of oil feed flow rate on the hydrogenation selectivity of soybean oil was investigated by performing SPE reactor experiments at oil feed flow rates between 80 and 400 mL/min, in the presence and absence of a nickel mesh turbulence promoter that was placed in the oil feed channel (in a blank test with no Pd catalyst, the Ni mesh was shown to have no catalytic activity for electrohydrogenation of soybean oil). From the width (0.28 cm) and depth (0.17 cm) of the oil channel, the range of oil flow rates translated into average linear velocities between 14 and 141 cm/s. For these experiments, the cathode catalyst was composed of 2.0 mg/cm^2 Pd-black, the current collector was Toray carbon paper 0.17 mm in thickness, and the operating temperature, pressure, and current density were fixed at 60°C, 1.0 atm, and 0.10 A/cm^2, respectively.

The fatty acid profiles, fatty acid hydrogenation selectivities, current efficiencies, and *trans* isomerization selectivities of oil products from these experiments are listed in Table 2. SLn, SLo, and SO increased monotonically with increasing oil flow rate, with and without the turbulence promoter. For example, SLo increased from 0.96 at a flow rate of 80 mL/min without a turbulence promoter to a value of 2.65 at 400 mL/min with a turbulence promoter. A significant decrease in stearic acid content (from 25.6 to 12.2%) was observed with increasing oil turbulence/flow velocity, with a $C_{18:3}$ concentration in the hydro-oil products of ≤3%. There was some loss in the efficiency of hydrogen addition to the oil at the highest oil flow rate, but the current efficiencies did not correlate with oil flow velocity/turbulence. The selectivity results suggest that a high oil flow rate and/or turbulence

was facilitating oil mass transfer out of the Pd catalyst bed, thus shortening contact times of oil with the catalyst surface and decreasing the extent of fatty acid saturation. The modest increase in SI with increasing flow rate was associated with the improvement in hydrogenation selectivity.

Next, we sought to determine whether the physical thickness of an MEA's cathode catalyst layer might affect fatty acid hydrogenation selectivities (i.e., whether a thinner bed would decrease the residence time of oil in contact with the catalyst). Although we were unable to directly measure the thickness of the cathode catalyst layer (because some catalyst material penetrated into the Nafion membrane and carbon paper current collector during the hot-pressing step of MEA fabrication), we did know that the thickness would increase with increasing Pd-black loading on the carbon sheet current collector (for constant temperature and pressure conditions during hot-pressing). Thus, soybean oil hydrogenation experiments were carried out with cathode catalyst loadings between 0.25 and 10.0 mg/cm^2. Toray carbon paper (0.17 mm in thickness) was used as the cathode and anode current collector, and the operating temperature, pressure, and current density were fixed at 60°C, 1.0 atm, and 0.10 A/cm^2, respectively.

As shown in Table 3, all three fatty acid hydrogenation selectivities, as well as the specific isomerization selectivity, increased with decreasing catalyst loading. The results indicate that the residence time of oil in the cathode layer (short residence times for thin layers) influenced strongly the extent of fatty acid hydrogenation. It is important to note that the local current density on the Pd particles increased as the catalyst

TABLE 2
Effect of Oil Flow Rate on Soybean Oil Hydrogenation Selectivity and *cis/trans* Isomerization for Pd Catalyst[a]

	Flow rate (mL/min)	Fatty acid profile (%)				IV	Current efficiency (%)	SLn	SLo	SO	SI
		$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$						
Without	80	25.6	30.7	29.7	2.9	85	59	1.35	0.96	1.30	0.16
turbulence	180	22.7	32.8	29.8	3.0	88	69	1.31	1.11	1.46	0.16
promoter	296	22.4	35.5	28.3	2.5	86	72	1.44	1.33	1.90	0.20
	400	13.1	38.1	34.6	3.0	101	50	1.68	1.95	3.27	0.22
With	80	20.8	37.5	27.6	2.4	86	71	1.44	1.52	2.19	0.18
turbulence	180	14.5	38.6	32.2	2.9	97	56	1.53	1.85	2.83	0.21
promoter	296	17.7	40.5	28.8	1.9	90	66	1.80	1.93	3.47	0.23
	400	12.2	41.8	32.6	2.3	98	53	1.89	2.65	5.03	0.26

[a]Cathode: 2.0 mg/cm^2 Pd-black, 10% Nafion, 10% PTFE, Toray carbon paper backing (0.17 mm thickness); current density: 0.10 A/cm^2; temperature: 60°C; pressure: 1.0 atm. For abbreviations and manufacturers see Table 1.

TABLE 3
Effect of Cathode Catalyst Loading on Soybean Oil Hydrogenation Selectivity and *cis/trans* Isomerization[a]

Catalyst loading (mg/cm^2)	Fatty acid profile (%)				IV	Current efficiency (%)	SLn	SLo	SO	SI
	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$						
0.25	8.7	35.8	40.3	4.0	111	34	1.46	2.17	3.16	0.24
0.5	13.9	39.1	32.8	2.9	98	45	1.58	2.00	3.16	0.20
1.0	17.5	39.8	29.1	2.5	91	53	1.49	1.87	2.80	0.18
1.5	17.7	36.6	31.3	3.1	94	54	1.37	1.51	2.07	0.17
2.0	25.6	30.7	29.7	2.9	85	59	1.35	0.96	1.30	0.16
10.0	37.4	26.9	22.2	1.7	66	49	1.27	0.85	1.08	0.11

[a]Cathode: Pd-black, 10 wt% Nafion, 10 wt% PTFE, Toray carbon paper backing (0.17 mm thickness); current density: 0.10 A/cm^2; flow rate: 80 mL/min; temperature: 60°C; pressure: 1.0 atm. For abbreviations and manufacturers see Table 1.

loading decreased (even though the apparent current density based on the geometric MEA area was constant) because there was less catalyst surface area for electrochemical hydrogen generation. Since the results in Table 1 show that changes in current density had no effect on hydrogenation selectivities, we have ruled out the possibility that variations in hydrogen concentration on the Pd were the root cause of the SLn, SLo, and SO selectivity trends in Table 3. With regard to the oil hydrogenation current efficiency, the optimal catalyst loading was 1.0 or 2.0 mg/cm^2. At lower catalyst loadings, the local current density was high and excessive amounts of H$_2$ gas were produced (the same effect is shown in Table 1). At a high catalyst loading of 10 mg/cm^2 the oil hydrogenation current efficiency was also low due to slow mass transfer (primarily diffusion) of triglyceride molecules into and out of the Pd-black layer, which could not keep pace with the electrogeneration of hydrogen. The trend of decreasing *trans* isomerization with increasing catalyst loading in Table 3 was associated with the increase in saturated fatty acid content of oil products from a high catalyst loading experiment.

The influence of oil mass transport through the carbon sheet current collector on oil product selectivities was quantified by examining a series of carbon paper and carbon cloth backing materials with different thicknesses (ranging from 0.09 to 1.0 mm) and porosities (78–91%). The results from these experiments are listed in Table 4. A general increase in SLn, SLo, and SO with increasing carbon paper/cloth porosity was observed. On the other hand, there was no correlation of selectivity with current collector thickness. The current efficiency decreased slightly when the hydrogenation selectivity increased, indicating that it may be possible to control the extent of hydrogen addition to unsaturated fatty acids without sacrificing the efficiency of hydrogen addition. The value of SI was either 0.14 for low-selectivity experiments (with oil products containing ≈24% stearic acid) or ≈0.27 for high-selectivity electrolyses with stearic acid contents of 13–14%. The best cathode backing material, in terms of hydrogenation selectivity, was the CDC (knitted carbon cloth) with a thickness of 1.0 mm and a porosity of 89%.

Modified cathode catalysts. Another approach for improving the performance/selectivity of a noble metal hydrogenation catalyst is to add various modifiers or promoters (8). Bimetallic Pd catalysts, for example, have been used to improve the selectivity of the chemical catalytic hydrogenation of acetylene to ethylene and butadiene to 1-butene (9). In our study, bimetallic cathode MEA were investigated, where a second metal (either Ni, Cd, Zn, Pb, Cr, Fe, Ag, Cu, or Co) was electrodeposited *in-situ* on Pd-black after MEA fabrication. Our rationale for adding the second metal was to alter the adsorption characteristics of triglycerides on the catalyst, thereby shortening the time of catalyst/oil contact which, in turn, should decrease the amount of saturates in the hydro-oil product.

To fabricate a bimetallic cathode MEA, sheets of Nafion 117 membrane were first immersed in a salt solution [Ni(NO$_3$)$_2$, CdSO$_4$, ZnSO$_4$, Pb(NO$_3$)$_2$, CoSO$_4$, FeSO$_4$, Cr(NO$_3$)$_3$, or CuSO$_4$ at a concentration of 0.25 M, or 0.5 M AgNO$_3$] for 12 h, during which time the H$^+$ counter ions in Nafion (i.e., those cations associated with the membrane's SO$_3^-$ ion exchange sites) were exchanged by metal cations from the external salt solution. After salt equilibration, the membranes were thoroughly washed with deionized and distilled water to remove cations (and their accompanying anions) not associated with the membrane's fixed charges. The treated Nafion membranes were then used as the solid polymer electrolyte for MEA fabrication, using the general procedure described in the Experimental Procedures section of this paper. After hot-pressing anode and cathode powders to the membrane (with Toray TCP17 carbon paper anode and cathode current collectors), the MEA was mounted in the SPE reactor and N$_2$ gas was pumped through the cathode compartment feed channel while deionized and distilled water was circulated past the anode. The reactor was then operated at a constant current density of 1.31 mA/cm^2 to displace membrane metal ions with electrogenerated H$^+$, transport the metal ions to the cathode, and electrodeposit the metal onto the Pd-black powder (2.0 mg/cm^2 Pd). Metal plating was continued for sufficient time to allow all metal ions inside the membrane to be electrochemically reduced on the Pd cathode (a total charge of 10.6 coulombs accomplished this task). The cath-

TABLE 4
Effect of Cathode Backing Materials on Soybean Oil Hydrogenation Selectivity and *cis/trans* Isomerization[a]

| Carbon backing material[b] | Fatty acid profile (%) | | | | | Current efficiency | | | | |
	C$_{18:0}$	C$_{18:1}$	C$_{18:2}$	C$_{18:3}$	IV	(%)	SLn	SLo	SO	SI
TCP17	25.6	30.7	29.7	2.9	85	58	1.35	0.96	1.30	0.16
TCP09	23.7	29.0	32.6	3.5	91	56	1.15	0.85	0.97	0.14
SCP	17.8	36.4	32.1	2.6	94	52	1.52	1.44	2.19	0.23
CAC	17.0	36.6	32.5	2.8	95	51	1.45	1.48	2.15	0.23
CDC	12.7	39.1	34.3	2.8	100	53	1.58	2.03	3.21	0.26
SCPM	14.2	39.1	32.6	2.7	97	48	1.51	1.88	2.83	0.27

[a]Cathode: 2.0 mg/cm^2 Pd-black, 10% Nafion, 10% PTFE; current density: 0.10 A/cm^2; temperature: 60°C; pressure: 1.0 atm; flow rate: 80 mL/min.
[b]TCP17—Toray TGPH-060 carbon paper; porosity = 0.78, thickness = 0.17 mm (Toray Industries, Inc.; Tokyo, Japan; available from E-TEK, Inc., Natick, MA); TCP09—Toray TGPH-030 carbon paper, porosity = 0.81; thickness = 0.09 mm (Toray Industries, Inc.); SCP—Spectracarb 2050A-1040 carbon paper, porosity = 0.82; thickness = 0.25 mm (Spectracorp, Ltd.; available from E-TEK, Inc., Natick, MA); CAC: plain weave carbon cloth, porosity = 0.85, thickness = 0.35 mm (E-TEK, Inc.); CDC—knitted carbon cloth, porosity = 0.89; thickness = 1.0 mm (E-TEK, Inc.); SCPM—Spectracarb 2050A-2020 carbon paper, porosity = 0.9, thickness = 0.51 mm (Spectracorp Ltd.).

TABLE 5
Fatty Acid Profile and Total *trans* Isomers Content for Modified Pd Catalyst[a]

	Fatty acid profile				Current efficiency		
Added metal	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	IV	(%)	SI
Without modifying	25.6	30.7	29.7	2.9	85	59	0.16
Cr	6.7	32.8	44.7	4.7	118	21	0.35
Fe	5.9	38.1	41.3	3.5	114	23	0.35
Co	9.9	46.6	30.4	1.9	98	42	0.32
Ni	12.9	41.6	31.2	2.7	97	44	0.27
Cu	8.8	42.1	35.0	2.8	104	35	0.27
Zn	6.3	31.5	45.8	4.9	119	26	0.20
Ag	15.6	41.1	29.4	2.4	93	50	0.27
Cd	5.5	31.5	47.0	4.8	121	23	0.26
Pb	4.5	27.7	51.0	5.3	126	16	0.42

[a]Cathode: 2.0 mg/cm^2 Pd-black, 10% Nafion, 10% PTFE, Toray carbon paper backing (0.17 mm thickness); current density: 0.10 A/cm^2; temperature: 60°C; pressure: 1.0 atm; flow rate: 80 mL/min. For abbreviations and manufacturers see Table 1.

ode loading of the second metal was approximately 3.4 mg/cm^2 for Ag, 1.8 mg/cm^2 for Cd, 1.7 mg/cm^2 for Pb, and 0.9–1.0 mg/cm^2 for Ni, Co, Fe, Zn, Cr, and Cu. After the metal reduction step, RB soybean oil was circulated past the cathode and a normal batch-recycle oil electrohydrogenation experiment was carried out (at 60°C, atmospheric pressure, and an oil flow rate of 80 mL/min).

Fatty acid profiles, hydrogenation current efficiencies, and specific SI for nine bimetallic cathodes are listed in Table 5. Current efficiencies and hydrogenation selectivities for the same cathodes are presented in Figure 2. Three striking results are obvious from these data: (i) all three fatty acid hydrogenation selectivities increased after addition of the second metal; (ii) oil products contained very low amounts of stearic acid (8.8–15.6%) and linolenic acid (1.9–2.8%), even though the oil feed flow rate was low and the porosity of the carbon paper current collector was low; and (iii) the hydrogenation current efficiencies with the modified cathodes were lower than those observed with pure Pd-black. Not surprisingly, based on the high unsaturated fatty acid content of the oil products, more *trans* isomers were produced with the se-

lective bimetallic cathodes, with values of SI 1.25–2.6 times greater than those for a pure Pd cathode.

Based on the results in Figure 2 an additional set of soybean oil hydrogenation experiments was performed with Pd-black cathodes containing Cu, Co, and Fe (these transition metal modifiers showed the best performance, in terms of low stearic acid content, low linolenic acid content, and reasonably high current efficiencies). For these electrolyses the modifier loading was fixed at ~1.0 mg/cm^2 and the Pd-black loading was varied from 0.0 mg/cm^2 to 2.0 mg/cm^2. Toray TCP17 carbon paper was used for the cathode current collector, and the reactor temperature, pressure, and current density were set at 60°C, 1.0 atm, and 0.10 A/cm^2. The results of these experiments are presented in Table 6. When the cathode contained only the transition metal (no Pd), there was essentially no change in the fatty acid profile (current efficiencies ≤3%), indicating that the electrodeposited metal had no catalytic properties for soybean oil hydrogenation in the SPE reactor. Although the SLn, SLo, and SO selectivities with Fe were the highest of the three cathode modifiers, the hydrogenation current efficiencies with iron were quite low and never greater than 23%. The Cu- and Co-modified cathodes worked very well, with current efficiencies in the range of 30–43%, and $C_{18:0}$ contents of 6.3–9.9% for oil products with 1.9–3.2% linolenic acid. The optimal Pd-black loading was 1.0-2.0 mg/cm^2 for a Cu or Co loading of 1.0 mg/cm^2. The specific SI were not significantly different from those found in high flow rate and porous current collector experiments (see Tables 2 and 4).

In two final soybean oil hydrogenation experiments, we combined two or more of the conditions discussed above that improved the hydrogenation selectivity. Soybean oil was hydrogenated at a cathode composed of Co (1.0 mg/cm^2) that was deposited on Pd-black (1.0 or 2.0 mg/cm^2) with a CDC carbon cloth current collector. The oil feed flow rate was either 180 mL/min (with a turbulence promoter) or 80 mL/min (no turbulence promoter), the temperature was 60°C, and the applied current density was 0.10 A/cm^2. As shown by the fatty acid profiles and SLn, SLo, and SO data in Table 7, the selectivity improvements presented in the prior sections of this
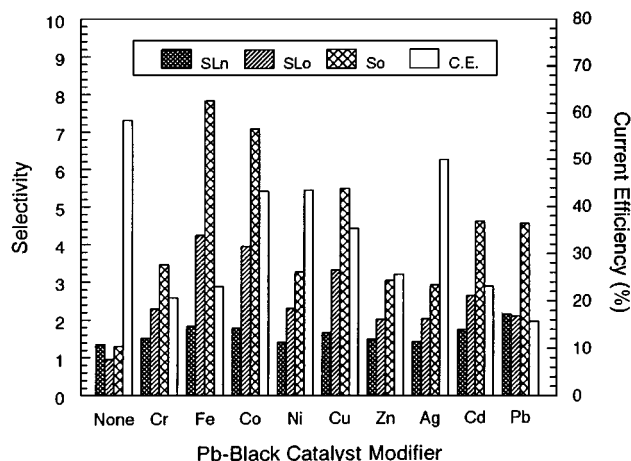
FIG. 2. Oil hydrogenation selectivities and current efficiencies (C.E.) using a Pd-black catalyst cathode that was modified by the addition of a second metal.

TABLE 6
Effect of Modified Cathode Catalyst with Different Pd Loading on Soybean Oil Hydrogenation Selectivity and *cis/trans* Isomerization[a]

Modifier	Pd loading (mg/cm^2)	Fatty acid profile (%)				IV	Current efficiency (%)	SLn	SLo	SO	SI
		$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$						
Cu	2.0	8.8	42.1	35.0	2.8	104	35	1.66	3.32	5.49	0.27
	1.5	7.4	40.7	37.3	3.2	108	31	1.62	3.60	5.83	0.27
	1.0	7.9	45.3	33.3	2.1	102	38	1.91	4.49	8.60	0.29
	0.5	6.5	39.6	39.3	3.2	111	29	1.81	3.91	7.08	0.28
	0.0	3.8	22.3	55.3	7.3	134	2	—	—	—	0.0
Co	2.0	9.9	46.6	30.4	1.9	98	43	1.79	3.95	7.08	0.32
	1.5	6.9	44.0	35.4	2.5	106	34	1.85	5.09	9.42	0.27
	1.0	6.3	41.0	38.5	2.9	110	30	1.91	4.62	8.82	0.29
	0.5	6.0	37.4	42.2	3.0	113	19	2.30	3.67	8.43	0.34
	0.0	3.7	22.4	55.5	7.3	135	3	—	—	—	0.0
Fe	2.0	5.9	38.1	41.3	3.5	114	23	1.84	4.24	7.82	0.35
	1.5	5.9	40.5	40.1	2.5	111	22	2.38	5.33	12.7	0.32
	1.0	6.1	42.2	38.3	2.1	108	20	2.46	5.21	12.9	0.35
	0.5	6.0	40.3	40.1	2.3	110	16	2.54	4.67	11.9	0.36
	0.0	3.7	22.1	55.7	7.4	135	3	—	—	—	0.0

[a]Cathode: Pd-black, 10% Nafion, 10% PTFE, Toray carbon paper backing (0.17 mm thickness); current density: 0.10 A/cm^2; temperature: 60°C; pressure: 1.0 atm; flow rate: 80 mL/min. For abbreviations and manufacturers see Table 1.

TABLE 7
Combination of Selectivity Improvement Effects[a]

Cathode conditions	Fatty acid profile (%)				IV	Current efficiency (%)	SLn	SLo	SO	SI
	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$						
2.0 mg/cm^2 Pd and 1.0 mg/cm^2 Co CDC current collector 80 mL/min oil feed flow rate	6.4	41.8	38.1	2.6	109	41	2.06	4.99	10.3	0.34
1.0 mg/cm^2 Pd and 1.0 mg/cm^2 Co CDC current collector 180 mL/min oil feed flow rate oil feed turbulence promoter	5.3	38.5	42.5	2.3	113	29	2.93	4.85	14.2	0.40

[a]Current density: 0.10 A/cm^2; temperature: 60°C; pressure: 1.0 atm. For abbreviations see Tables 1 and 4.

paper were not completely additive. Nevertheless, we were able to further improve fatty acid selectivities by combining a highly porous CDC current collector with a Pd/Co cathode (where, for example, SLo was found to be 10.3 vs. a value of 7.0 in Table 6), with only a modest increase in the *trans* isomers (an SI value of 0.40 in Table 7 vs. 0.32 in Table 6).

Comparison with chemical catalytic reaction schemes. Based on the above results, we can now assign reaction conditions and MEA designs for the synthesis of partially hydrogenated soybean oils with low, moderate, and high fatty acid hydrogenation selectivities. The products from such SPE reactor experiments compare well with literature data for the chemical catalytic hydrogenation of soybean oil at a Ni or Pd catalyst in a slurry or fixed bed reactor (Table 8). For oils hydrogenated electrochemically at moderate or high selectivity conditions, SLn, SLo, and SO were generally higher and SI values were lower than those from a chemical catalytic scheme with Pd. Although the hydrogenation selectivities with a Ni catalyst for an IV 110 oil were greater than those from the electrochemical process with a Pd/Co cathode (high selectivity conditions), the final fatty acid profiles for the two cases were nearly identical (i.e., the $C_{18:0}$ and $C_{18:3}$ were essentially

the same) and the final *trans* isomer content with Pd/Co was less than half that with Ni. For oil products with similar fatty acid profiles, the *trans* isomer content using the SPE reactor was always less than that formed in a chemical catalytic reaction scheme. For example, an IV 75 soybean oil, hydrogenated with a Ni catalyst, had a $C_{18:0}$ content (12%) and a $C_{18:1}$ + $C_{18:2}$ content (71 + 5.5%) that were similar to those of an IV 98 oil hydrogenated electrochemically under moderate selectivity conditions. The electrohydrogenated oil, on the other hand, had one-fourth the concentration of *trans* isomers, again showing clearly an important advantage of the SPE reactor method. In general, the range of *trans* isomer content for the low, moderate, and highly selective SPE reactor conditions was narrow (6.5–9.5%) for a rather broad spread in product IV, and the *trans* content did not increase significantly when the electrochemical hydrogenation reaction was more selective (the isomerization index did increase by a factor of 1.5, but this was due to differences in the IV of the oil products). Electrohydrogenated oils with fatty acids profiles intermediate to those in Table 8 (e.g., an oil with 18% $C_{18:0}$) can be produced, of course, by proper interpolation of the SPE reactor conditions and/or bimetallic cathode composition.

TABLE 8
Comparison of Chemical Catalytic and Electrochemical/Solid Polymer Electrolyte (SPE) Reactor Soybean Oil Hydrogenation[a]

	Fatty acid profile (%)								
	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	IV	SLn	SLo	SO	SI (% *trans*)
SPE reactor—low selectivity 2.0 mg/cm^2 Pd TC17 current collector 80 mL/min oil feed flow rate (1)	23.8	28.9	32.5	3.6	91	1.24	0.84	1.04	0.15 (6.5)
SPE reactor—moderate selectivity 2.0 mg/cm^2 Pd TC17 current collector 400 mL/min oil feed flow rate with turbulence promoter	12.2	41.8	32.6	2.3	98	1.89	2.65	5.03	0.27 (9.1)
SPE reactor—high selectivity 1.0 mg/cm^2 Pd and 1.0 mg/cm^2 Co CDC current collector 180 mL/min oil feed flow rate with turbulence promoter	5.3	38.5	42.5	2.3	113	2.90	4.85	14.2	0.40 (9.5)
Chemical catalytic hydrogenation Ni catalyst in a slurry reactor; 140°C/44 psig (6)	4.8	43.4	38.0	2.9	110	1.84	11.3	20.8	0.80 (20)
	12.0	71.0	5.5	0.0	75	—	—	—	0.65 (39)
0.5% Pd/Al$_2$O$_3$; 80°C/17.8 psig; fixed bed reactor (11)	12.2	26.9	43.4	5.4	110	1.62	0.75	1.22	0.37 (8)
1% Pd/C; 170°C/50 psig; fixed bed reactor (12)	10.2	33.2	39.5	5.6	112	0.80	1.40	1.12	0.81 (17)
5% Pd/C; 60°C/27.5 psig; slurry reactor (13)	4.3	34.1	43.9	5.3	118	1.70	8.3	14.1	1.59 (22.2)

[a]SPE reactor operated at 60°C, 1 atm pressure, and 0.10 A/cm^2 current density. For abbreviations see Tables 1 and 4.

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