(54) MEMBRANE ELECTRODE ASSEMBLY FOR A FUEL CELL

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(57) ABSTRACT

A catalyst ink for a fuel cell including a catalytic material and poly(vinylidene fluoride). The ink may be applied to a substrate to form an electrode, or bonded with other electrode layers to form a membrane electrode assembly (MEA).

8 Claims, 2 Drawing Sheets
FIG. 1
FIG. 2

Cell Voltage (V)

Current Density (mA/cm²)

60°C, 1.0 M MeOH, 20 psig O₂

83°C 20 psig O₂
1.0 M Methanol
In one aspect, the invention is a catalyst ink for a fuel cell including a catalytic material and poly(vinylidene fluoride).

In another aspect, the invention is a process for making a catalyst ink for a fuel cell, including mixing components including a catalytic material and poly(vinylidene fluoride).

The catalyst ink may be applied to a surface of a substrate to form an electrode for a fuel cell assembly. The substrate may be a membrane or a backing.

The electrode with the deposited ink layer may be bonded with a membrane or another electrode at a temperature greater than about 180°C to form a membrane electrode assembly (MEA).

The MEA with the deposited ink layer may be incorporated into a fuel cell stack.

The catalytic ink of the invention improves the interfacial bonding characteristics of the deposited electrocatalytic layers with the proton conducting moieties of the membrane structure, which improves the electrical performance and reduces the impedance compared to MEAs made with conventional inks. The catalytic ink of the invention also reduces methanol crossover when used in a fuel cell stack.

MEAs made with the catalytic inks of the invention demonstrate good electrical performance, excellent crossover characteristics, and unique water management properties when evaluated at the cell level.

The details of one or more embodiments of the invention are set forth in the accompanying drawings and the description below. Other features, objects, and advantages of the invention will be apparent from the description and drawings, and from the claims.

DESCRIPTION OF DRAWINGS

FIG. 1 is schematic cross sectional view of a direct feed fuel cell.

FIG. 2 is a plot of cell voltage vs. current density that compares the performance of a conventional membrane electrode assembly to that of a membrane electrode assembly of the invention.

Like reference symbols in the various drawings indicate like elements.

DETAILED DESCRIPTION

FIG. 1 illustrates a liquid feed organic fuel cell having anode 110, cathode 120 and solid polymer proton-conducting cation-exchange electrolyte membrane 130, preferably made of a perfluorinated proton-exchange membrane material available from E. I. duPONT de Nemours, Wilmington, Del., USA, under the trade designation NAFION. NAFION is a co-polymer of tetrafluoroethylene and perfluorovinylether sulfonic acid. Other membrane materials can also be used.

Anode 110, cathode 120 and solid polymer electrolyte membrane 130 are bonded to form a single multi-layer composite structure, referred to herein as membrane-electrode assembly “MEA” 140.

A fuel pump 150 is provided for pumping an organic fuel and water solution into anode chamber 160. The organic fuel and water mixture is withdrawn through outlet port 170 and recirculated. Carbon dioxide formed in anode chamber 160 is vented through outlet port 180 within the tank 190. An air compressor 1100 is provided to...
feed oxygen or air into a cathode chamber 1120. Carbon
dioxide and water are removed through a port 1140 in the
cathode chamber 1120.

Prior to use, anode chamber 160 is filled with the organic
fuel and water mixture. Cathode chamber 120 is filled with
air or oxygen either at ambient pressure or in a pressurized
state. During operation, the organic fuel in anode chamber
160 is circulated past anode 110. Oxygen or air is pumped
into cathode chamber 120 and circulated past cathode 120.
When electrical load 1130 is corrected between anode 110
and cathode 120, electro-oxidation of the organic fuel occurs
at anode 110 and electro-reduction of oxygen occurs at
cathode 120. The occurrence of different reactions at anode
110 and cathode 120 give rise to a voltage difference
between these two electrodes.

Electrons generated by electro-oxidation at anode 110 are
conducted through external load 1130 and are captured at
cathode 120. Hydrogen ions or protons generated at anode
110 are transported directly across membrane electrolyte
130 to cathode 120. A flow of current is sustained by a flow
of ions through the cell and electrons through external load
1130.

The cathode 120 is a gas diffusion electrode in which
unsupported or supported platinum particles are bonded to
one side of the membrane 130. In the process of the
invention, a catalytic composition, referred to herein as a
catalyst ink, is applied to at least one surface of the mem-
brane 130 or to at least one surface of an electrode
backing material.

The cathode 120 and the anode 110 are gas diffusion
electrodes in which electrocatalyst particles are bonded to
at least one side of the membrane 130. To make the cathode
120 and the anode 110, an electrocatalytic composition,
referred to herein as a catalyst ink, is applied to at least one
surface of the membrane 130 or to at least one surface of an
electrode backing material.

For the cathode 120, the catalytic material may be in the
form of fine metal powders (unsupported), or dispersed on
high surface area carbon (supported), and is preferably
unsupported platinum black, fuel cell grade, available from
Johnson Matthey Inc., USA or supported platinum materials
available from E-Tek Inc., USA. The loading of the alloy
particles in the electrocatalyst layer is preferably in the range
of about 0.5 mg/cm² to about 4.0 mg/cm². More efficient
electro-oxidation is realized at higher loading levels.

The electrocatalyst in the anode 110 is formed from
supported or unsupported platinum-ruthenium particles.
A bimetallic powder, having separate platinum particles and
separate ruthenium particles gives better results than plat-
num-ruthenium alloy. In a preferred embodiment, the plat-
num and ruthenium compounds are uniformly mixed and
randomly spaced throughout the material, i.e., the material
is homogeneous. This homogeneous bimetallic powder is
used as the anode catalyst material. The preferred ratio of plati-
num to ruthenium can be between 60/40 and 40/60.
The desired performance level is believed to occur at 60%
platinum, 40% ruthenium. Performance degrades slightly as
the catalyst becomes 100% platinum. Performance degrades
more sharply as the catalyst becomes 100% ruthenium.
For platinum-ruthenium, the loading of the alloy particles in
the electrocatalyst layer at preferably in the range of about 0.5
mg/cm² to about 4.0 mg/cm². More efficient electro-oxidation is
realized at higher loading levels.

The catalyst ink may also include an ionomer to improve
ion conduction and provide improved fuel cell performance.
Ionomer materials perfluorosulfonic acid, e.g., NAFION,
only or in combination with TEFLO-N. A preferred form for
the ionomer is a liquid copolymer of perfluorovinylether
sulfonic acid and tetrafluoroethylene. To improve the per-
formance of PSSA-PVDF membranes, PVDF is added to the
catalyst ink, preferably in a powder form.

While not wishing to be bound by any theory, it is
believed that the formation of the proton conducting
channels at the interface of the PSSA-PVDF membrane and
deposited catalyst layer is governed by inter-miscibility of
the various polymers. Conventional catalyst inks included
only NAFION ionomer. However, NAFION and PVDF-
PSSA do not have similar properties, and the entropy of
mixing between these to polymers is not favorable. There-
fore, to improve the miscibility between the polymers in
the catalyst ink and the membrane, it is important add a com-
patible ionomeric material to the catalyst ink so that the
deposited catalyst layer acquires properties similar to the
membrane. PVDF having a low intrinsic permeability to
methanol will result in low crossover through the anode
structure into the membrane.

In addition, since PSSA-PVDF membranes do not swell
significantly in water, they do not have the desired plasticity
when the membrane is bonded to the electrodes under hot
pressing conditions. The use of a high boiling solvent in
the catalyst ink, such as, for example, N,N-dimethylacetamide
(DMA), provides a plasticizing effect. The use of N,N-
dimethylacetamide (DMA) and other solvents also prevents
membrane dry-out during the MEA fabrication process and
thereby result in an MEA that is has a lesser tendency to
der-laminate.

The catalyst ink is preferably applied directly on at least
one side of a substrate such as the membrane 130 or on an
electrode backing material to form a catalyst-coated elec-
trode. Suitable backing materials include, for example, car-
bon fiber papers manufactured by Toray Industries, Tokyo,
Japan. These carbon papers are preferably “Teflonized”
to be about 5 wt % in Teflon.

The application process includes spraying or otherwise
painting the catalyst ink onto the substrate, with both the ink
and the substrate at or substantially near room temperature.
No high temperature treatment step is required to activate
the hydrophobic particles in the catalyst ink solution. After
drying on the substrate, the loading of the catalyst particles
onto the substrate is preferably in the range of about 0.5
mg/cm² to about 4.0 mg/cm².

The application of the catalyst ink on to the membrane is
significantly improved if the membrane surface is roughened
prior to application of catalyst ink. Surface roughening
provides additional anchoring sites for the catalyst and the
polymer.

The membrane may be roughened by contacting the
membrane surface with a commercial paper coated with fine
abrasive. The abrasive should preferably have a grit size in
the range of about 200 to about 400.

The abrasive material should be selected such that par-
ticles of the abrasive impregnated in the membrane are
tolerated by the fuel cell. Abrasives that are preferred are
silicon nitride, boron nitride, silicon carbide, silica and
boron carbide. Abrasive using iron oxide or aluminum oxide
should be avoided as these materials result contaminates
the membrane with metal ions leading to increased resistance
and this is undesirable.

Both sides of the membrane are roughened. The mem-
brane is then held in a fixture and preferably allowed to dry
before the catalyst ink is painted.

The anode 110, the membrane 130, and the cathode 120
may be assembled into the membrane electrode assembly
140. Once bonded together, the anode 110, cathode 120 and
membrane 130 form a single composite layered structure.
Preferably, the electrode and the membranes are first laid
or stacked on a CP-grade 5 Mil (0.013 cm), 12-inch (30.5 cm)
by 12-inch (30.5 cm) titanium foil to prevent acid from the
membrane from leaching into the electrode.
Improving the melt-flow characteristics of the polymer membrane during the hot pressing process enhances the interfacial bonding. TGA analysis indicates that PSSA-PVDF systems are relatively stable to about 220°C. In addition, conductivity measurements of membrane samples before and after being subjected to high temperature (up to about 200°C) suggest that loss of sulfonic acid groups (conducting moieties) does not occur under these conditions. Both of these aspects suggest that temperatures higher than about 180°C should be employed to improve the melt-flow characteristics of membrane sample, thus improving the interfacial bonding characteristics of the MEA.

The invention will now be further described with reference to the following non-limiting example.

EXAMPLE

Prior to deposition of the catalyst ink, PSSA-PVDF membrane samples were dried and the surface secured with 240 grade abrasive-coated paper to roughen the membrane surface for enhanced bonding characteristics.

The membrane sample was then sandwiched between two TFE (Teflon) blocks with a 2 inch (5 cm) x 2 inch (5 cm) window exposed. The membrane sample is then dried with a hand held blower for approximately 30 minutes or until the membrane surface is taut and dry.

Two different types of catalyst ink mixtures were prepared. The inks were applied to the membrane surface using a painting technique. A catalyst ink mixtures in Table 1 were applied to the surface of a TEFLONized backing paper available from Toray Industries, Tokyo, Japan. The backing paper was impregnated with about 5% by weight TEFLON.

The catalyst ink mixtures in Table 1 were applied to the anode and cathode sides of the membrane. Sonication was used to ensure adequate mixing of the components.

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ANODE</td>
<td>CATHODE</td>
</tr>
<tr>
<td>140 mg Pt/Ru</td>
<td>180 mg Pt</td>
</tr>
<tr>
<td>400 mg H2O</td>
<td>400 mg H2O</td>
</tr>
<tr>
<td>720 mg NAFION</td>
<td>720 mg NAFION</td>
</tr>
<tr>
<td>(5 wt %)</td>
<td>(5 wt %)</td>
</tr>
<tr>
<td>400 mg DMA</td>
<td></td>
</tr>
</tbody>
</table>

The catalyst ink mixtures in Table 2 were applied to the carbon papers. Sonication was used to ensure adequate mixing of the components.

<table>
<thead>
<tr>
<th>TABLE 2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ANODE</td>
<td>CATHODE</td>
</tr>
<tr>
<td>140 mg Pt/Ru</td>
<td>180 mg Pt</td>
</tr>
<tr>
<td>400 mg H2O</td>
<td>400 mg H2O</td>
</tr>
<tr>
<td>720 mg NaFION</td>
<td>720 mg NaFION</td>
</tr>
<tr>
<td>(5 wt %)</td>
<td>(5 wt %)</td>
</tr>
</tbody>
</table>

The catalyst ink prepared for the membrane was applied to the membrane surface using a painting technique. A coating of DMA/H2O solution was painted on the membrane edges. A titanium plate was inserted on the top of the membrane and a copious amount (5–7 ml) of water was added to the die. The top plate was then inserted and the die was then placed into a hot press.

Once the die was inserted into the press the die plate was closed with a force of 2000–2500 lbs (909.1–1136 kg) over a 36 cm2 area electrode. The die was heated to a temperature of 180–185°C for a period of 15 minutes and then cooled using an automated chiller. Following this procedure, the die was opened and the MEA removed and assembled into a cell for evaluation.

The conditions of testing, for the results shown in FIG. 2, were similar except for the temperature. It is important to remember that increasingly higher temperatures leads to improved performance in methanol fuel cells. The results demonstrate that the process of the invention leads to a higher fuel cell performance. Comparing curve I and curve II, the voltage at 150 mA/cm2 is increased by about 0.1 V, and the improvement at higher current densities is more than 0.2 V.

The electrical performance of fuel cells employing membrane-electrode assemblies prepared by the process of the invention was measured and their performance compared with MEAs prepared by conventional processes. These results are shown in FIG. 2 for 1.0 M MeOH and 20 psig O2. Curve I shows fuel cell performance using an MEA prepared by the process of the invention, while curve II represents an otherwise identical fuel cell using an MEA prepared by a conventional process. The results demonstrate that the process of the invention confers the value of the process of the invention.

The membrane of claim 1, wherein the catalytic material comprises Pt.

The membrane of claim 1, wherein the catalytic material comprises Pt and Ru.

The membrane of claim 1, wherein the catalyst ink comprises the second ionomer.

The membrane of claim 1, wherein the catalyst ink comprises a liquid copolymer of tetrafluoroethylene and perfluorovinylethersulfonic acid.

The membrane of claim 1, wherein the catalyst ink comprises a plasticizer.

The membrane of claim 1, wherein the plasticizer is N,N dimethylacetamide.

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