Inkjet printable anode ink for fuel cell applications

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Abstract

Passive Direct Methanol Fuel Cells (DMFC) are stand-alone power sources that consist of anode and cathode sandwiched between electrodes. Typically the catalyst layer consists of carbon, platinum and ruthenium particles. Platinum and ruthenium are the catalysts and carbon particles provide electrical conductivity. The catalyst and proton-conducting Nafion can be formulated into a printable ink. We present experiments for formulation of inkjet printable stable inks containing the catalyst and Nafion solution. When printed on suitable substrates the inks can provide layers suitable to be used as a part of membrane electrode assemblies (MEAs) of a DMFC device. Two formulations have been successfully manufactured and inkjet printed with laboratory scale printheads: a water based ink and a solvent based ink. The water based ink was compatible with also industrial scale printheads thus providing possibility for process upscaling. However, the solvent based ink is considered to have more potential in DMFC devices since it requires no surfactant that might interfere with the electrochemical reactions.

Background

Passive Direct Methanol Fuel Cells (DMFC) are small stand-alone power sources. They are a subcategory of proton-exchange fuel cells in which methanol is used as the fuel. Their main advantage is the ease of transport of methanol that is an energy-dense yet reasonably stable liquid at all environmental condition. DMFCs are targeted especially to portable applications due to the quite low efficiency of DMFCs. In portable applications energy and power density are more important than efficiency.

In DMFC, methanol is oxidized catalytically at the anode producing electrons and protons. The protons migrate to the cathode through a proton exchange membrane and react catalytically with oxygen to produce water. The electrons are transported through an external circuit from the anode to the cathode thus providing power to connected devices. At the anode, methanol and water are adsorbed on a catalyst usually made of platinum (Pt) and ruthenium (Ru) particles, and lose protons until carbon dioxide is formed.

Typical structure of DMFC is anode and cathode sandwiched between electrodes. The anode of DMFC can be printed in order to enable flexible structure, tailored performance and cost-effective manufacturing process. The printed anode contains both proton- and electron-conducting materials, and a catalyst, and can be used as a part of MEA (membrane electrode assembly) combining both anode and cathode functionalities. Typical target characteristics for the printed anode are passive operation at room temperature with 1 M methanol. Printing processes can also be used for the other layers of the DMFC device, such as for making printed electrodes, printed dielectric layer and lamination (Figure 1).

Inkjet printing is a potential method for printed electrodes since it has low material consumption essential when using expensive materials such as Pt. Inkjet printing also enables printing of multiple ink layers thus providing possibility for increase in layer conductivity without complicating the printing process. Lesch et al have in their recent review evaluated the suitability of inkjet printing as a fabrication method for electrochemical devices, such as fuel cells [1].

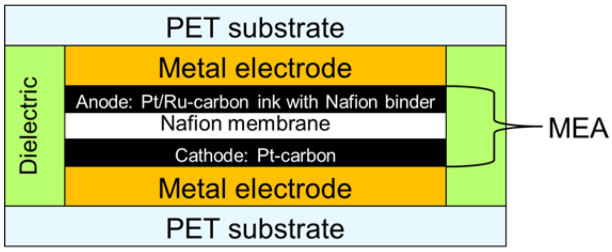

Figure 1. *Layers for a printed 1-cell DMFC device.*

Towne et al have formulated a stable water based ink based on Pt/C catalyst and Nafion solution for use as a MEA in a polymer electrolyte membrane fuel cell (PEMFC) [2]. Printing was carried out with off-the-shelf office printers. They achieved similar MEA performance compared to commercial MEAs. Taylor et al have also evaluated inkjet printable MEAs for PEMFC fabrication based on Pt/C catalyst [3]. They used methanol as the main ink solvent for an inkjet ink printable with an office printer.

This paper describes formulation and printability of an inkjet printable anode ink for application as part of MEA in a flexible DMFC device that has 5 cells operating with 0.3 V at 8 mA cm^{-2} each. The ink is based on proton-conducting Nafion and conductive carbon black nanoparticles together with Pt and Ru particles (C-Pt/Ru). Two inks – 1) a water based and 2) a solvent based – were formulated and inkjet printed on Nafion film and carbon paper. Both laboratory-scale and industrial-scale inkjet printheads were used for evaluation of printability. VTT has long experience in formulation of inkjet printable functional inks and this expertise was used in selection of the solvent vehicle and optimization of ink properties [4]. VTT has also experience in development of enzyme based bio fuel cells [5].

Materials and methods

Commercial mixture of carbon black, Pt and Ru was used as the catalyst (Platinum wt-% 27-31, Ruthenium wt-% 14-16.5, on carbon black XC-72R) from Quintech (C-Pt/Ru).

Three Nafion solution candidates were used:

- Nafion 1: 10 wt-% Nafion solution in water (eq. wt. 1000) from Sigma-Aldrich
- Nafion 2: 10 wt-% Nafion solution in water (eq. wt. 1100) from Sigma-Aldrich
- Nafion 3: 5 wt-% Nafion perfluorinated resin solution in lower aliphatic alcohols and 15-20 % water from Sigma-Aldrich

For the water based ink distilled water and 1,2-propandiol were used in the solvent vehicle. Non-ionic surfactant Dynol 604 from Air Products Chemicals was added to optimize the surface tension of the ink. For the solvent based ink diacetone alcohol was used as the main solvent.

For printing two inkjet printers were used (Figure 2): 1) laboratory scale multinozzle inkjet printed based on single use printhead cartridges (Fujifilm Dimatix DMP-2831, 10 pl drop size), and 2) laboratory scale multinozzle printer (PiXDRO LP50) with industrial printheads (Fujifilm Dimatix SE-128, 30 pl drop size).

Figure 2. *DMP-2831 and LP50 inkjet printers.*

Nafion film with 183 µm thickness (Nafion 117 membrane from Fuel Cells Etc) and 190 µm thick carbon paper (Toray carbon paper 060 from Fuel Cell Store) were used as substrates. Photographic paper (Intelicoat Technologies) was used as a reference substrate.

For ink characterization surface tension and viscosity were measured. Surface tension was measured with Aqua Pi Instrument from Kibron Inc. Viscosity was measured with Anton Paar MCR-301 rheometer at +20 ^{o}C.

Layer resistance of the printed samples was measured with a standard multimeter at 2 cm measuring distance between the electrodes.

For sheet resistance 4-point probe measurement (principle in Figure 3) was used. This is required when the substrate itself is conductive, such as carbon paper. In the principle a certain current (this case 10 mA) is fed to the sample. If the same current can be measured the sample is conductive and the voltage is then also measured.

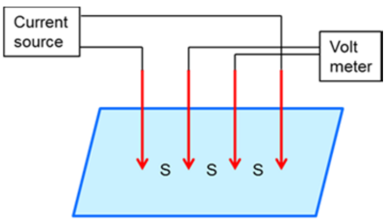

Figure 3. *Principle of 4-point probe measurement for sheet resistance. S is needle spacing. The edges of the sample should be 4*S.*

The sheet resistance can be calculated based on the equation when the probes are at a distance of S of each other and the edges of the sample are 4S (1):

$$\rho_s = \frac{V}{I}\frac{\pi}{\ln 2} = \frac{V}{I}4.5324 \qquad (1)$$

where

ρ_s = sheet resistance (Ω/sq)

V = voltage between the inner probes (V)

I = current through the outer probes (A)

Results

Ink formulation

The solvent vehicle for the water based ink was mixed from water and 1,2-propandiol (2:1) with 0.05 wt-% surfactant. The different Nafion solutions 1-3 were mixed with the solvent vehicle with 10 wt-% resulting in three formulations. The viscosity and surface tensions of the three formulations were 5 cP / 47.3 mN/m (Nafion 1), 4.2 / 49.3 mN/m (Nafion 2) and 6.2 cP / 37.6 mN/m (Nafion 3). Ink formulation from Nafion 1 was unstable during surface tension measurement, and formulation from Nafion 2 had too a high surface tension probably due to high water content in the Nafion 2 solution. As a result Nafion 3 was chosen for further experiments.

For final formulation 10 wt-% of Nafion 3 solution and 0.5 wt-% of C-Pt/Ru particles were added to the solvent vehicle thus resulting in 1:1 relation between Nafion and C-Pt/Ru. No other additives were used. The formulation was sonicated 15 minutes and afterwards magnetically stirred 16 hours resulting in a stable and a homogenous ink. The ink was filtered with 5 µm. Also 1 µm filtering was tested, but the C-Pt/Ru particles were too large (Figure 5). The recommended particle size for the printers is smaller than 1 µm. However, since the nozzle diameter is 27 µm with 10 pl, it was estimated that the too large particle size might be acceptable without clogging the nozzles due to its stable behavior outside the printer. The viscosity of the ink was measured to be approximately 4.5 cP and surface tension 37.5 mN/m. The optimal inkjet ink requirements for the printers used are 8-20 cP and 24-36 mN/m. The formulation had properties slightly outside the optimal range, but it was still expected to be inkjet printable and further formulation wasn't carried out.

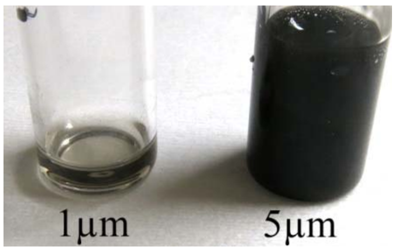

Figure 4. *Water based ink filtered with 1 µm and 5 µm filters.*

The solvent based ink consisted of diacetone alcohol, 10 wt-% of Nafion 3 solution and 0.5 wt-% of C-Pt/Ru particles, without any additives or a surfactant. The formulation was sonicated 15 minutes and afterwards magnetically stirred 16 hours resulting in a stable and homogenous ink. The ink was filtered with 5 µm, and again 1 µm filtering didn't work. The viscosity of the ink was measured to be approximately 5 cP and surface tension 30 mN/m thus showing ideal surface tension, but slightly too small ink viscosity.

Specific viscosities for the both water and solvent based inks at some shear rates are presented in Table 1.Viscosity curves of the both inks are presented in Figure 5 both showing almost Newtonian behavior ideal for inkjet printing.

Table 1. Viscosity (cP) for the water based and the solvent based ink at specific shear rates.

Shear rate (1/s)	Water based ink	Solvent based ink
1	4.72	5.40
10	4.53	5.21
100	4.48	5.19
1000	4.41	5.02
5000	4.37	4.83

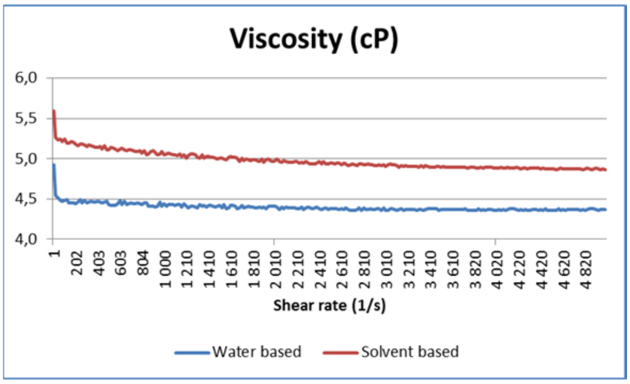

Figure 5. *Viscosity curves for the water based and the solvent based inks.*

Printing

Both inks were inkjet printed with DMP-2831 printer at printhead temperature +25 ^{o}C and they showed good drop formation and printability with 1270 dpi (Figure 6). Square of 2 cm was used as a print layout.

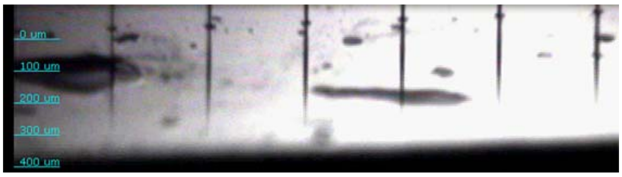

Figure 6. *Drop formation of the water based ink with DMP-2831 printer.*

The water based ink was printed on the photographic paper and carbon paper and different amounts of ink layers were used, namely 1, 2, 3 and 5 ink layers. The ink was compatible with the both substrates providing good print quality and adhesion. Nafion film was also tested as a substrate, but due to high water content of the ink, the water sensitive Nafion film started to wrinkle during printing. Increasing the substrate temperature during printing up to +50 ^{o}C didn't offer a solution to wrinkling. Wrinkle of Nafion substrate was one motivation for development of a solvent based ink. Another motivation was a concern that the surfactant might interfere with the electrochemical performance by adhering to Pt particles. Due to these concerns the solvent based ink was printed on the Nafion film with 5 ink layers providing good print quality and adhesion without substrate wrinkling. Microscopic images (50x magnification) of the printed areas are presented in Figure 7.

Figure 7. *Inkjet printed samples on different substrates: from left 1) water based ink on Nafion film, 2) solvent based ink on Nafion film, 3) water based ink on carbon paper (darker area on left).*

The water based ink was also printed with LP50 printer that uses industrial scale printheads in order to give estimations on upscaling of the formulation from laboratory scale to industrial scale. Photographic paper was used as a substrate and 1, 2 and 3 ink layers were printed with 500 dpi resolution. Printability with industrial scale printheads was good at a printhead temperature of +25 ^{o}C.

Measurement of sheet resistance

Layer resistance of the water based ink was measured on photographic paper. There was no conductivity with 1 ink layer, but 2 and 3 ink layers provided resistance of 22.3 Ω and 35.5 Ω, respectively. Sheet resistance of the water based ink on carbon paper was measured by using the 4-point probe principle from the sample with 5 ink layers resulting in 0.008 V voltage and 3.59 Ω/sq sheet resistance. With 1-3 ink layers on carbon paper the samples were not conductive when comparing to the pure carbon paper. Due to substrate wrinkling the samples on Nafion film were also not conductive.

Layer resistance of solvent based inks was measured on photographic paper and on Nafion film. With five ink layers the measured resistance was 2.9 MΩ and 0.8 MΩ, respectively. There was no conductivity with less ink layers.

The measured layer resistance with the solvent based ink was significantly higher than with the water based ink. The solvent based ink requires further development of the ink and printing process, specifically increase in catalyst and carbon content and in the amount of ink layers. However, the both inks look promising for passive DMFC development since it is possible to produce stable conductive catalyst inkjet inks.

Conclusions

Water based and solvent based inks have been formulated to be used for fabrication of MEAs for passive DMFC. The formulations are based on C-Pt/Ru as a catalyst and Nafion solution. Stable ink formulations have been successfully manufactured and inkjet printed on different substrates. Electrical performance has been measured from the printed layers in order the layers to potentially perform as a part of MEAs. The solvent based ink formulation is the most promising one, because besides carbon paper it is compatible also with Nafion film as a substrate, but further formulation and printing process optimization is required. Another advantage is that the solvent based formulation doesn't require any surfactant for surface tension optimization. Surfactants, even non-ionic ones, have potential to interfere with electrochemical performance of the electrodes. Thus it is recommended to focus on formulations without surfactants or perhaps even without other typical inkjet ink additives.

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