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Citation	Journal of The Electrochemical Society, 168(10), 104504 <a href="https://doi.org/10.1149/1945-7111/ac2684">https://doi.org/10.1149/1945-7111/ac2684</a>
Issue Date	2021-10-22
Doc URL	<a href="http://hdl.handle.net/2115/88597">http://hdl.handle.net/2115/88597</a>
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Type	article (author version)
File Information	43826_J2104-157991-Uemura_1st_edit_TrackedCopy_uemura_rev4_clear.pdf



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**Title: Reaction products affecting the PEFC catalyst ink property**

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**Abstract**

Catalyst ink is a key material of the catalyst layer in a proton exchange membrane fuel cell, but can be degraded as the reactions of alcohols are promoted by Pt in the ink. The present study quantitatively determined the concentrations of reaction products in an ethanol/water-based catalyst ink, and the effects of these substances on the ink and catalyst layer were investigated. The acetaldehyde concentration was found to be the key factor, as acetaldehyde caused particle agglomeration in the catalyst ink and micro-scale crack formation in the catalyst layer.

## Introduction

The catalyst layer (CL) in a proton exchange membrane fuel cell is one of the most critical components determining the cell performance. CLs are typically fabricated on a commercial scale using the decal method [1] and are made from a catalyst ink mixed with platinum-supported carbon (Pt/C), an ionomer solution and a solvent. The catalyst ink is applied to a sheet or membrane as a coating and then dried to form the CL. Various aspects of this process, from the initial characteristics of the catalyst ink to the drying technique, will determine the structure of the CL as well as the performance of the fuel cell. Thus, it is important to control the quality of the catalyst ink to obtain a uniform, high performance CL [2].

Many studies have focused on the dispersion state of the catalyst ink because it affects the CL quality and the cell performance. In order to clarify the dispersion state of Pt/C and ionomers, catalyst ink has been investigated by using viscosity measurement, dynamic light scattering, small-angle X-ray scattering, and TEM [3-5]. As a result, several factors were found that affect the dispersion state. One of them is the solvent composition of the catalyst ink. When using the different type of alcohol or changing the alcohol concentration, the catalyst layer structure and cell performance were changed remarkably [6-8].

On the other hand, the authors found that the alcohol reacts due to the catalytic action of the Pt during the catalyst ink fabrication and changes into other substances [9-11]. Since the reaction occurs unintentionally in the fabrication process, the amount of reaction products and its effect on the dispersibility of Pt/C and ionomer are not clear. Therefore, the present study quantitatively assessed the concentrations of the various reaction products using GC/MS, and the effects of these substances on the catalyst ink were evaluated by measuring viscosity and particle size distribution. The results of these investigations elucidated the interactions and dispersion states of the substances generated in the ink. The quality of CLs fabricated from various catalyst ink samples were also investigated using microscopy.

## Experimental

The catalyst inks were prepared using a combination of water and ethanol (EtOH, Wako Pure Chemical Industries, Ltd., Osaka, Japan) as the dispersant. These inks also contained a

Pt catalyst supported on carbon black (TEC10V30E, Pt loading: 30 wt%, Tanaka Kikinzoku Kogyo K.K., Tokyo, Japan) together with Nafion® DE1021 (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan). In the various ink specimens, the ethanol:water ratio was set to 20:80, 46:54 or 60:40 on a mass basis. Because previous studies have shown that the catalytic action of Pt generates reaction products from alcohols, it was expected that the levels of such products and the properties of the catalyst ink would change upon varying the initial ethanol concentration [9, 10]. In each formulation, the nonvolatile content was 10 wt% while the Nafion® : carbon support mass ratio was 0.75.

All substances were not mixed together at once. After weighing the Pt/C, water, Nafion® solution, and ethanol were weighted and added in this order. Premixing was performed each time the material was added. For premixing, a planetary centrifugal mixer (ARE-310, THINKY, Tokyo, Japan) was used. Mixing time was set to 1 min and the rotation speed was 2,000 rpm. The samples premixed catalyst inks were processed in a high-speed rotary type mixer (Filmix, PRIMIX, Hyogo, Japan) that applied a shearing force intended to produce a nanometer-scale slurry. Mixing time was set to 10 min and it was operated at 22,000 rpm (shearing speed:  $15000\text{ s}^{-1}$ ). The container was water-cooled and the temperature was kept in the range of 20 to 30 °C.

The effects of reaction products were assessed by also producing a pseudo ink based on carbon black (VULCAN XC72, CABOT, Boston, MA, USA) instead of the Pt supported on carbon black. This sample was made using the same formulation and procedure as the catalyst ink but leaving out the Pt to avoid promoting oxidation and condensation reactions of the ethanol. Carbon and ionomer were set to the same content as the catalyst ink.

The composition of the liquid component of each formulation was analyzed by GC/MS (GCMS-QP2020NX, SHIMADZU, Kyoto, Japan). In this process, the Pt/C was first removed by centrifugation and only the liquid phase (still containing the Nafion®) was examined, with quantification based on pre-constructed calibration curves. In addition, the viscosity of each fresh catalyst ink or pseudo ink was measured using a vibration-type viscometer (VM-10A, SEKONIC, Tokyo, JAPAN). The diameter distribution of the Pt/C aggregates in each catalyst ink was ascertained using a laser scattering particle size distribution analyzer (LA-960V2, HORIBA, Kyoto Japan). This device was able to determine the particle size distribution of

the catalyst ink without dilution of the sample, based on the transmittance of light laser at a visible wavelength through an ink sample contained in a narrow glass cell with 2  $\mu\text{m}$  gap. The measurement performance of this measuring device conforms to the ISO13320 standard, and the measurement accuracy for standard particles (NIST-traceable mono and polydisperse size standards) is  $\pm 0.6\%$ . The dispersion state of each catalyst ink was also visualized by microscopy (ECLIPSE LV-N, Nikon Corporation, Tokyo, Japan) and images were acquired using a high-resolution camera (DS-Ri2, Nikon Corporation, Tokyo, Japan) [10].

We also considered the time required from catalyst ink fabrication to analysis. Since the measuring process is simple, viscosity, particle size distribution measurements, and microscope observation were performed immediately after the ink preparation. For GC/MS analysis, the pretreatment centrifugation process took 1 to 2 hours. However, the previous study suggests that the reaction does not progress remarkably unless strong stirring [9].

After the catalyst inks were characterized as above, CLs were fabricated by applying each ink to a polytetrafluoroethylene (PTFE) sheet using a doctor blade with a gap of 100  $\mu\text{m}$  followed by drying under ambient air. The quality of each CL was subsequently investigated by using the same microscopy technique as the catalyst ink observation.

## Results and Discussion

The physical properties of the catalyst ink were investigated while varying the initial ethanol concentration, and Figure 1 shows the viscosities of the resulting specimens. Several viscosity characteristics (pseudo ink, ethanol solution containing no solids, Nafion solution (Nafion<sup>®</sup> concentration: 3 %, solvent composition: ethanol 46%, water 54%)) are also shown for comparison with the catalyst ink. The ink and pseudo ink viscosity values were increased relative to that of the ethanol solution as a result of adding the solid contents (Pt/C, carbon, and Nafion<sup>®</sup>). As the initial ethanol concentration was varied from 0% to 46%, both the catalyst ink and pseudo ink exhibited similar changes in viscosity that were qualitatively consistent with the viscosity variations of the ethanol solution and Nafion<sup>®</sup> solution. However, while the viscosity of the pseudo ink at 60% ethanol continued to exhibit a similar trend to that of the ethanol solution and Nafion<sup>®</sup> solution at 60% ethanol, the viscosity of the catalyst ink increased significantly.

In order to discuss the result of viscosity measurement, it is necessary to consider the characteristics of the viscometer. Since the viscometer uses an ultrasonic vibrator, measurement conditions are almost similar to those measured in the high shear region of the rotary viscometer. It is considered that present measurement was performed with collapsing the loose agglomeration structure. Thus, the overlap of the two plots indicates that the catalyst ink and the pseudo ink were almost in the same dispersion state when the loose agglomerate structure was collapsed [12]. However, when the initial ethanol concentration reached 60%, the catalyst ink showed remarkably higher viscosity than the pseudo ink. It suggests that a strong agglomeration structure was formed in the catalyst ink.

The viscosity change of the catalyst ink is ascribed to variations in the dispersion state of the Pt/C and Nafion®. Thus, the particle size distributions were determined, as shown in Figure 2. At an initial ethanol concentration of 20% in the catalyst ink, the particles exhibited a monodisperse distribution with a median size of 0.18  $\mu\text{m}$ . The variation in median size was  $0.17 \pm 0.01 \mu\text{m}$  when the ink was made three times. In the case of the sample containing 46% ethanol, the median size increased slightly to 0.24  $\mu\text{m}$  and the distribution changed to polydisperse. The particle size distribution was significantly broadened and the median size was increased in the catalyst ink with 60% ethanol. Here, it should be noted that the detection of large agglomerates in the ink. Agglomerates larger than 2  $\mu\text{m}$  in bulk are compressed and flattened in the narrow glass cell and detected on the order of 10-100  $\mu\text{m}$  in diameter. However, the qualitative trend of increasing median size suggests the formation of agglomeration, and it corresponds to the viscosity increase shown in Figure 1. Compared to the catalyst ink, the particle size distribution of the pseudo ink with an initial ethanol concentration of 60% was monodisperse and the median size was almost the same as that of the catalyst ink with an initial ethanol concentration of 20%.

From the results of viscosity and particle size distribution, it can be seen that the characteristics of the catalyst ink change drastically only when Pt is contained under high ethanol concentration conditions. Previous study has shown that the presence of Pt affects the rheological properties of catalyst ink [13]. On the other hand, under the condition that a solvent with a high alcohol concentration and Pt coexist, the amount of reaction products generated in the ink will also increase. It is possible that the reaction product also affects the

dispersibility. Thus, GC/MS analysis was performed ~~used~~ to assess the reaction products in the catalyst inks. Specifically, the compositions of the specimens with initial ethanol concentrations of 46% and 60%, which had a significant difference in viscosity, were analyzed. Three major reaction products were found in both catalyst inks: acetaldehyde, acetic acid, and ethyl acetate. Previous studies have demonstrated that these substances are generated by the oxidation and condensation reactions of ethanol [10]. Figure 3 compares the concentrations of each product in the two catalyst inks. It was found that under current ink production conditions, several reaction products are generated on the order of %. The acetaldehyde was generated at the highest concentration. In addition, when the initial ethanol concentration in the catalyst ink was increased from 46% to 60%, only the acetaldehyde concentration was greatly increased.

Looking back at the results shown in Figures 1 to 3, they are closely related and two notable points are suggested. First, the deterioration of dispersibility and the viscosity increase may be due to the solid agglomeration caused by the reaction products in the catalyst ink. Second, the reaction products may have affected agglomeration in the catalyst ink when they reached a certain concentration. Based on the result of concentration measurement, the characteristics of the catalyst ink can be changed significantly when the acetaldehyde concentration exceeds the threshold value. Previous studies have already reported the effect of the interaction of platinum, carbon, ionomers and solvents (ethanol and water) on the characteristics of the catalytic inks [13]. Present results suggest that there is also effect of reaction product in addition to those reported interactions.

In order to investigate the effect of each reaction product, an experiment was conducted using a modified catalyst ink. Those inks were simulated a state in which the oxidation or condensation reactions of the ethanol had progressed in a sample having a good dispersion state with an ethanol concentration of 46%. The modified catalyst inks were prepared by intentionally adding the various reaction products (that is, acetaldehyde, acetic acid, and ethyl acetate) while reducing the ethanol concentration in the catalyst ink from the original value of 46% by an amount corresponding to the quantity of the additive.

Figure 4 presents the results of viscosity measurement and microscopic observation of the normal and modified catalyst ink, and the CL prepared from those inks. Prior to each

analysis, the catalyst ink sample was injected between two glass plates with a gap of 2  $\mu\text{m}$ , while the CL specimens were formed on PTFE sheets. In Figure 4(a), the normal catalyst ink exhibits a dispersion state assumed from the particle size distribution in Figure 3. That is, the catalyst ink with an ethanol concentration of 46% is seen to have dispersed almost homogeneously (Figure 4 (a)-1). In contrast, the catalyst ink with an ethanol concentration of 60% (Figure 4(a)-2) showed inhomogeneous dispersion and displayed black regions representing microscale agglomerates along with white regions where light was able to pass through the solvent.

The quality of each CL was correlated with the properties of the catalyst ink. Many micro-scale cracks were generated when using the poorly dispersed ink with an ethanol concentration of 60%. This is in agreement with previous studies, which have suggested that agglomerates can trigger crack generation [10, 14]. An increase in the coating thickness of the catalyst ink also causes crack formation [14, 15]. However, since the thickness of both catalyst layers was almost the same as 7-8  $\mu\text{m}$ , the effect of coating thickness can be negligible in this study.

The normal catalyst ink with an ethanol concentration of 46% did not cause cracks in the CL, although the modified catalyst inks showed various differences. Specifically, the addition of acetaldehyde caused agglomerates to form in the ink such that cracks were generated in the CL (see Figure 4(b)). Small aggregates were formed following the addition of 2% acetaldehyde, but with only a few pin holes observed in the CL. In contrast, 5% acetaldehyde produced a dispersion state of the catalyst ink and a CL morphology very similar to those obtained with the normal catalyst ink containing 60% ethanol (Figure 4(a)-2). The amount of acetaldehyde contained in this modified ink was almost equivalent to that found in the sample with a 60% initial ethanol concentration, and the quality of the ink and CL were very similar. From these results, it is apparent that an acetaldehyde concentration exceeding a threshold value in the range of 2% to 5% generated a large number of cracks in the CL.

Interestingly, increasing the acetic acid concentration had little effect on the dispersion of the catalyst ink or the quality of the CL, which remained very good (Figure 4(c)). Even an acetic acid level of 10%, which was much higher than the concentrations determined in the actual samples using GC/MS, did not cause any apparent quality changes. When only 1%



ethyl acetate was added, the dispersion of the ink did not deteriorate and the quality of the CL remained unchanged. The extent of ink dispersion was reduced at a level of 10% (Figure 4(d)-2). However, this concentration of ethyl acetate was significantly higher than the results obtained from the GC/MS analyses, and the number of cracks in the CL was lower than when acetaldehyde was added. Therefore, although ethyl acetate lowered the quality of the catalyst ink and the CL, the ethyl acetate concentration in the normal catalyst ink did not reach a level that would be expected to affect the product quality.

These results indicated that acetaldehyde is a key factor that causes agglomeration in the catalyst ink and cracks in the CL. In contrast, acetic acid had little effect. Thus, stabilizing the properties of the catalyst ink and maintaining the quality of the CL require careful control over the concentrations of reaction products. Further studies are needed on the correlation between the poor dispersion of the catalyst ink and the crack formation pattern in the CL. As shown in this study, the solvent of the fabricated catalyst ink contains many substances as a result of reaction. The solvent composition may change in the drying process due to the difference in evaporation rate for each substance. As a result, it can affect the CL formation process.

## Conclusions

The effects of reaction products generated in a catalyst ink on the properties of the ink and the quality of the associated CL were investigated. Acetaldehyde, acetic acid, and ethyl acetate were all detected in a catalyst ink sample using GC/MS. The concentrations of these substances were determined and acetaldehyde was found to be present on the order of several percent based on mass. When the initial ethanol concentration was increased from 46% to 60%, the acetaldehyde concentration increased remarkably and the agglomeration of Pt/C and Nafion® in the catalyst ink along with the ink viscosity were also greatly increased. The effects of the catalyst ink properties on the CL quality were investigated. The catalyst ink with a high acetaldehyde concentration showed poor dispersion, and many cracks were generated in the CL. From these results, the amount of acetaldehyde formed as a product of the reaction of ethanol likely significantly affects the catalyst ink properties and CL quality.

## Acknowledgments

The results reported herein were obtained under the PEMFC Research and Development Program “Highly-Coupled Analysis of Phenomena in MEA and its Constituents and Evaluation of Cell Performance”, commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

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## Figure Captions

Figure 1. Viscosity as a function of ethanol concentration for the catalyst ink, pseudo ink and

281 ethanol solution.

282 Figure 2. Particle size distributions in the catalyst ink with three ethanol concentrations.

283 Figure 3. The concentrations of reaction products in the catalyst ink at various initial ethanol  
284 concentrations.

285 Figure 4. Images obtained using microscopy showing the dispersion states in the catalyst ink  
286 samples and the quality of the resulting CLs.

287

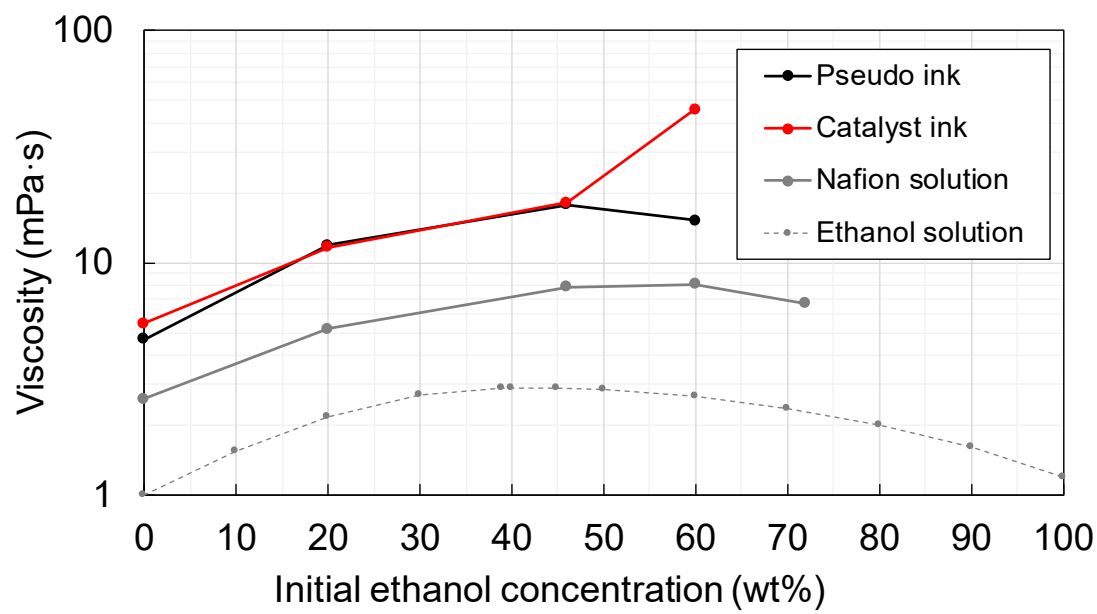


Figure 1. Viscosity as a function of ethanol concentration for the catalyst ink, pseudo ink, Nafion® solution and ethanol solution.

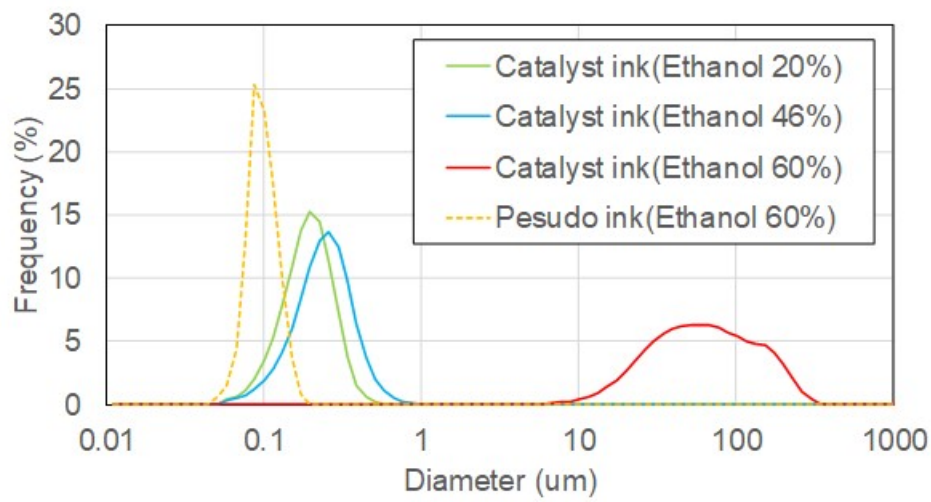


Figure 2. Particle size distributions in the catalyst ink with three ethanol concentrations.

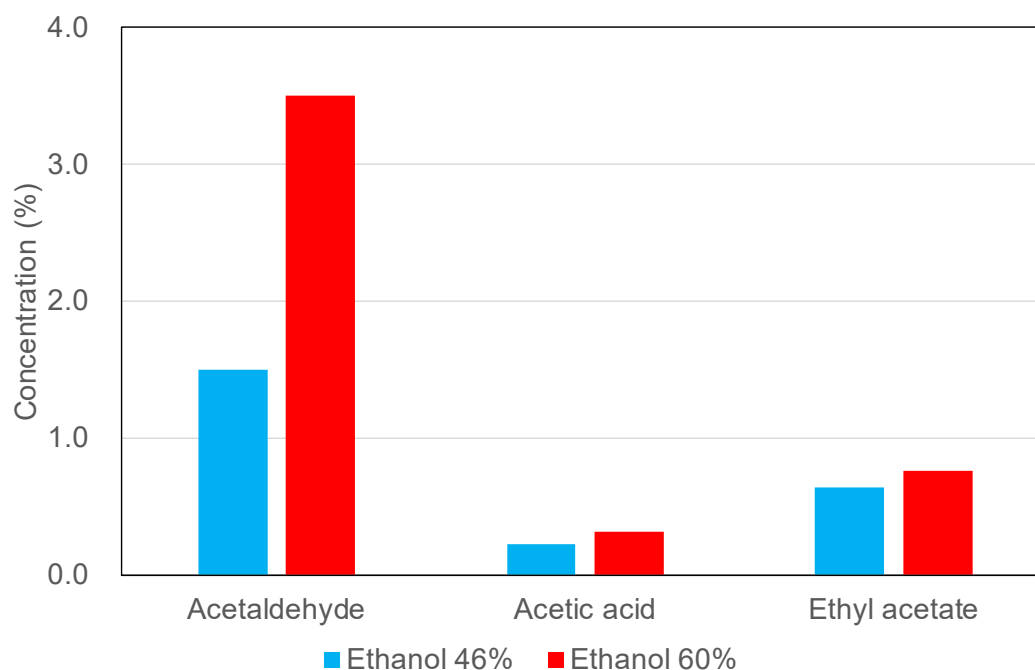


Figure 3. The concentrations of reaction products in the catalyst ink at various initial ethanol concentrations.

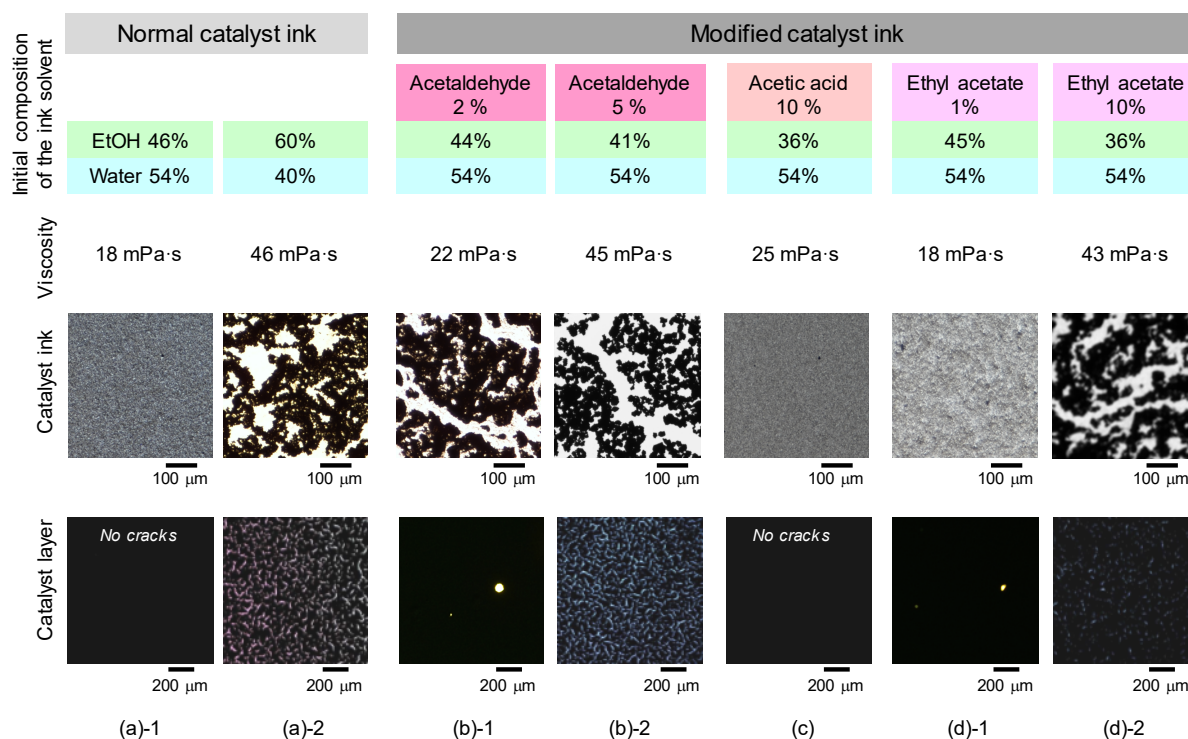


Figure 4. Images obtained using microscopy showing the dispersion states in the catalyst ink samples and the quality of the resulting CLs.