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Reusability of decal substrates for the fabrication of catalyst coated membranes

A. Stähler [a,*], M. Stähler [a], F. Scheepers [a], M. Carmo [a], D. Stolten [a,b]

[a] *Forschungszentrum Juelich GmbH, Institute of Energy and Climate Research, IEK-3: Electrochemical Process Engineering, 52425, Jülich, Germany*
[b] *Chair for Fuel Cells, RWTH Aachen University, Aachen, Germany*

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ABSTRACT

The use of decal substrates to produce catalyst coated membranes (CCMs) for polymer electrolyte membrane water electrolyzers or fuel cells is a common procedure. For economic and ecological reasons, the reuse of decal substrates would be desirable. Thus far, it has not been investigated whether reuse is possible. Therefore, this study focuses on the repeated coating and transfer in decal processes and investigates changes in substrate properties. After coating Kapton and PTFE with a Carbon-Nafion dispersion, the dry layer was transferred onto a Nafion membrane. This procedure was repeated 50 times. The change in substrate thickness and surface free energy (SFE), as well as the transfer rate (TR), were monitored. The residues on the substrate and scattering of the TR were higher for Kapton compared to PTFE. None of the decal substrates changed its SFE and thickness within the measurement uncertainties. Because of the smaller scattering in the TR, PTFE is more suitable for reuse.

1. Introduction

Catalyst coated membranes (CCMs) for polymer electrolyte membrane (PEM) electrolyzers or fuel cells can be produced in two ways. Either the catalyst dispersion is applied directly to the membrane or the decal transfer method [1–5] is used. In this method, the dispersion is first coated on a decal substrate or transfer film before the dried electrode is transferred to the membrane in a hot pressing or rolling process [6–8]. Afterwards, the decal substrate is no longer needed.

For ecological and economic reasons, the reuse of the decal substrates should be a goal. One important requirement for reusability is a complete transfer of the coating to the membrane [6,7], even after multiple uses of the decal film. In addition, a defect-free coating of the recycled decal film is an essential prerequisite. In order to meet these requirements, consistency of the substrate properties, such as surface free energy (SFE) during reuse, is required, as a change in the substrate's SFE, for example, could cause coating defects [9]. As no study has yet been published that investigates the reusability of decal substrates, this work addresses this issue.

The reuse of two widely-used decal substrates, namely glass fiber-reinforced (gfr) polytetrafluoroethylene (PTFE) and Kapton [6,7,10, 11] is analyzed herein. In order to avoid the use of valuable noble metal-containing catalysts, a dummy dispersion consisting of carbon and Nafion is used for the substrate coating. The dispersion is first applied to different samples, dried and then transferred via a hot pressing process on a membrane, as is customary for the decal process [1,6–8,12]. Subsequently, the completeness of the layer's transfer to the membrane is determined and defined as the transfer rate. Prior to a new coating and transfer cycle, the SFE and substrate thickness are measured. This process chain is repeated 50 times for each decal substrate sample.

2. Material and methods

All production and characterization experiments were performed in an air conditioned laboratory (temperature: 23 °C, relative humidity: 50%).

2.1. Dispersion preparation and characterization

For the catalyst dummy dispersion production, carbon prills (Cabot Vulcan XC72) were ground in a laboratory mill (A 10, IKA Labortechnik Staufen). The carbon material was mixed with deionized water, Nafion solution (D1021, Chemours Nafion content 11 wt%, water content 89 wt

* Corresponding author.
  E-mail address: a.staehler@fz-juelich.de (A. Stähler).

%) and 2-propanol (Sigma-Aldrich) (composition: carbon 6.5 wt%, water 62 wt%, 2-propanol 28 wt%, Nafion 3.5 wt%). The mixture was ultrasonically-dispersed (UW 3200, Bandelin electronic) and mixed with a laboratory stirrer (ViscoPakt Rheo-27, HiTec Zang GmbH). A subsequent degassing step in a vacuum reactor was applied to remove gas bubbles introduced during the manufacturing process or dissolved in the liquid phase.

The carbon dispersion was used for five coating cycles per day, with a new dispersion produced each day. To guarantee comparable coating properties, the viscosity flow curve, and the solid contents were monitored.

The flow curves of the dispersions were measured after the degassing step by using a rotational rheometer (MARS III, Thermo Fisher Scientific) with a cone plate geometry (diameter: 60 mm, angle: 2°). For the measurement, the shear rate was increased from 0.1 s^{-1} to 200 s^{-1} and then subsequently decreased again to 0.1 s^{-1} to ensure reproducible results. The solid content was determined by means of a moisture analyzer (M100, Sartorius) by drying 2 g of the dispersion to constant mass at 130 °C.

2.2. Decal film characterization

For the coating experiments, gfr–PTFE (Reichelt Chemietechnik) and Kapton HN (Dr. D. Müller Ahlhorn) were used. From each polymer film, three samples with dimensions of 140 mm × 70 mm were cut off. The thickness of each sample was measured in a 3 × 4 dot matrix with a spacing of 2 cm. For this purpose, a digital contact sensor GT2-A50 (Keyence, contact pressure: 16 N cm^{-2}) was used. To compare the thickness change over the different transfer cycles, the mean and standard deviation were formed over the 12 measurement points.

The grid-like SFE determination of the samples was performed using a large surface analyzer (LSA, Krüss GmbH) in combination with the accompanying software, ADVANCE1.7. The droplets of two different liquids, namely water (bidistilled and sterile, AppliChem) and diiodomethane (ReagentPlus®, 99%, Sigma-Aldrich) were deposited on the substrates and the contact angles were determined by means of the conic section method [13]. The 1.5 µl drops were placed in 3 × 4 dot matrix with a respective distance of 2 cm. The contact angle measurement of the two liquids allows calculating the polar and dispersive SFE of the substrates. The polar part is based on Coulomb interactions between permanent dipoles and between permanent and induced dipoles. The dispersive part is due to interactions based on temporal variations in the charge distribution of the atoms and molecules. The polar and dispersive components were calculated for each position in accordance with the approach of Owens and Wendt [14]. To reduce the influence of solvent impurities on the SFE calculation [15], the polar and dispersive parts of the water and diiodomethane were determined by a drop shape analyzer (DSA 30, Krüss GmbH). To control the SFE change across the transfer cycles, the mean and standard deviation were recorded over the 12 points.

The thickness and SFE measurements were repeated every fifth cycle.

2.3. Decal film coating and drying

Each of the decal substrate samples was coated with the carbon dispersion with a 50 mm single-layer slot die (TSE Troller AG). The laboratory scale set up used as described by Burdzik et al. [12]. The coating dimension was 5 cm × 12 cm, with a wet film thickness of 100 µm. The wet layer was dried at 80 °C in air, using a large scale thermal oil heated jet dryer (Coatema Coating Machinery GmbH).

Finally, the mass of each coated sample was measured using an analytical balance (AT201, Mettler-Toledo GmbH).

2.4. Transfer process

The dried layers were transferred on a Nafion 115 Membrane (Du Pont Fluoroproducts) by a hot pressing process. The three samples of the same type of decal film were positioned side by side on a sandwiched porous layer/silicone film/porous layer/Kapton. One Nafion 115 membrane with the dimensions of 210 mm × 140 mm was placed on the samples. A sandwich of Kapton/porous layer/silicone film/porous layer was placed on top of the membrane (see Fig. 1). In this way, the contact pressure was evenly distributed to all samples by the silicone layers and the porous intermediate layers prevented air pockets. The layer system was then placed between two steel plates (dimensions: 210 mm × 270 mm) and heated up to 130 °C in a hot press system (PWV 50 EH-SERVO, Paul-Otto Weber Maschinen-und Apparatebau GmbH). After the temperature was reached, the layer system was pressed for 3 min with 5 MPa. Then, the sandwich was cooled down to room temperature and the decal substrates were removed from the membrane by hand.

For the determination of the transfer rate, the weight of each sample was measured before and after the transfer by using an analytical balance (AT201, Mettler Toledo). Then, the samples were cleaned by using a damp cloth and, after ensuring that remaining water on the sample had been evaporated, the weight was again measured and used as a starting weight for the next coating cycle.

The transfer rates for each sample were calculated according to equation (1) by dividing the mass difference before and after the transfer step by the mass difference after drying and cleaning.

$$TR = \frac{m_{before\ transfer} - m_{after\ transfer}}{m_{before\ transfer} - m_{after\ cleaning}} \tag{1}$$

In order to reduce a measuring error in the mass determination by electrostatic charging, all samples were electrically discharged (Top Gun III, Simco-Ion) before the measurement was performed. The uncertainty of the transfer rate was calculated by means of Gaussian error propagation, with an uncertainty for the mass determination of 0.2 mg.

The coating and transfer process was repeated 50 times with each sample. The change of thickness and SFE of the substrate, as well as the transfer rates over the different cycles, was analyzed.

3. Results and discussion

3.1. Dispersion characterization

The investigation of the viscosity flow curves of the prepared carbon dispersions shows that the dispersions can be described by an Ostwald de Waele model: $\eta = m \cdot \dot{\gamma}^{n-1}$ [16], with the apparent viscosity η, the fluid consistency coefficient m, the shear rate $\dot{\gamma}$ and the flow behavior index n.

The fluid consistency m and flow index n are used as curve-fitting parameters. The flow index n of all produced carbon dispersions scatters in the range of 0.94 ± 0.02, the fluid consistency m in the range of 0.041 ± 0.005 Pas. All flow curves are presented in Fig. 2.

The solid content of the dispersions was also checked during the preparation of the different dispersions and was in the range of
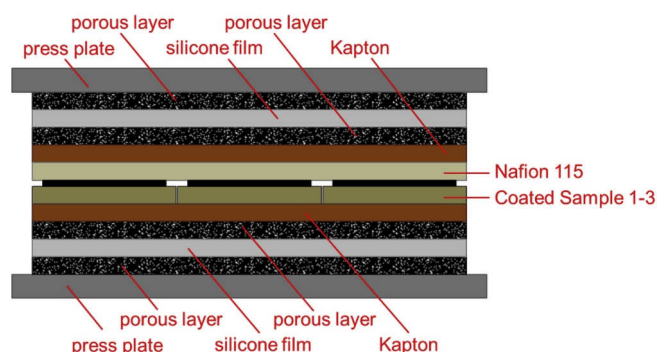

Fig. 1. Setup for the layer transfer during the hot-pressing process.

10.0±0.5 wt%.

3.2. Decal film characterization – initial film thickness and surface free energy

The decal substrate samples were analyzed for thickness and SFE at the beginning of the transfer cycles. The thickness of gfr-PTFE is in the range of $120\pm3\,\mu m$. The investigation of Kapton leads to a thickness of $126\pm2\,\mu m$.

For the SFE calculation, the polar and dispersion surface tension values of the water and diiodomethane used in this study were first determined by following the approach described by Burdzik et al. [15]. The resulting values for diiodomethane are $0.0\pm0.4\,mN\,m^{-1}$ as a polar part and $49.7\pm0.4\,mN\,m^{-1}$ as a dispersion part and, accordingly, for water $51.2\pm0.5\,mN\,m^{-1}$ and $21.3\pm0.5\,mN\,m^{-1}$.

The SFE calculation of the samples' surfaces after the initial contact angle measurement of water and diiodomethane gives a polar part for gfr-PTFE of about $0.1\pm0.1\,mN\,m^{-1}$ and a dispersion part of $12.5\pm1\,mN\,m^{-1}$. According to the three different Kapton samples the polar part of the SFE is in the range of $3.1\pm0.4\,mN\,m^{-1}$, the dispersion part in the range of $42.9\pm1.6\,mN\,m^{-1}$. The mean values and standard deviations of each sample are presented in Table 1.

3.3. Decal film thicknesses and surface free energies as a function of the cycle step

After every fifth transfer step of the coating from the decal substrate to the membrane, the measurement of the thickness and SFE was repeated. The results of the thickness measurement of gfr-PTFE and Kapton are shown in Fig. 3 as a function of the transfer step.

In the case of gfr-PTFE, within the uncertainty of the thickness measurement device, there is no significant change in the thickness values across the different cycles. For two of the three Kapton samples, a slight scattering of the thickness over the different cycles can be observed, but these are also indistinguishable within the scope of the uncertainty of the measurement.

The examination of the polar and dispersion SFE over the different transfer steps is summarized in Fig. 4 and Fig. 5.

The development of the SFE of the Kapton film shows no significant change in this property (see Fig. 4). The SFE scatters a little over the different transfer steps, while across the entire 50 transfer cycles, Kapton's polar SFE is in the range of $41.0\pm1.0\,mN\,m^{-1}$ and the dispersion part in the range of $4.9\pm0.9\,mN\,m^{-1}$. For this reason, no reuse impact on Kapton's SFE can be detected. In contrast to Kapton, the SFE evolution of

Fig. 2. Viscosity flow curves of the different carbon dispersion. The symbols represent the measured data and the line an Ostwald de Waele function, fitted to all measured data ($m = 0.041$ Pa s, $n = 0.94$).

| Sample | Thickness/µm | | Surface free energy/mN m^{-1} | | | |
| | | | polar | | dispersion | |
	Mean	stdev	Mean	stdev	Mean	stdev
gfr-PTFE S1	120	2	0.0	0.1	12.1	0.8
gfr-PTFE S2	118	1	0.1	0.1	12.7	1.1
gfr-PTFE S3	123	2	0.0	0.0	12.8	1.2
Kapton S1	126	2	3.1	0.3	43.0	1.4
Kapton S2	126	2	3.2	0.5	42.7	1.7
Kapton S3	126	1	3.1	0.3	42.9	1.6

gfr-PTFE shows a small conspicuousness after the first five cycles (see Fig. 5). The dispersion part of the SFE increases by about $2.5\,mN\,m^{-1}$ after the first five cycles. During the remaining 45 cycles, no significant change was observed, as the polar SFE is in the range of $15\pm1\,mN\,m^{-1}$. The situation for the disperse fraction is similar: After the first 5 cycles, the value increases slightly from 0 to $0.4\,mN\,m^{-1}$ and, for the remaining cycles, it scatters around $0.7\pm0.3\,mN\,m^{-1}$.

Why this change is observed cannot be clarified at this point. Coating and hot pressing seem to cause a change in the substrate's surface. Whether this change affects the essential in reuse, namely the transfer rate, is shown by the analysis of the transfer rate across the 50 cycles in the following.

3.4. Investigation of the transfer rate

Fig. 6 shows the course of the determined transfer rates for a gfr-PTFE (A) and for a Kapton sample (B) as a function of the transfer step number. Although intensive attempts were made to remove the electrostatic charge, it cannot be guaranteed that this was done completely in all steps. Thus, the distortion of the sample mass determination by means of the analytical balance can be affected by the remaining charge. It is assumed that the remaining electrostatic charge causes part of the scattering, especially for transfer rate values larger than 100%.

While for the gfr-PTFE samples, no trend in the transfer rate curves could be observed within the measurement uncertainty, the Kapton samples showed a stronger scattering that increases in two of the three samples with the increasing transfer step number. From about the 30th use of Kapton on, no reliable transfer of the coating to the membrane is possible.

For both decal films, outliers with lower transfer rate values can be observed. The outliers for gfr-PTFE (Fig. 6 (A), transfer step number 7 and 17) were related with an incomplete transfer in small, sharply defined areas (see Fig. 7 (A)). Outside of these areas, the carbon/Nafion layer has come off cleanly from the gfr-PTFE. For this reason, for gfr-PTFE samples, a cohesion break can be assumed.

In the case of the Kapton samples, not only small, sharply defined areas were observed. The samples also showed a gray haze over the entire coating area that clearly indicated failures of cohesion (see Fig. 7 (B)). The small, sharply defined areas and also the gray haze on the Kapton film could be easily removed with a damp cloth, but the emergence of these transmission errors cannot be prevented.

With increasing cycles, the TR gets worse and worse, but the adhesion of the coating in the edge areas gets better and better. This could be due to a change in the Kapton at the phase boundary. Eventually, the chemical resistance will be affected by the dispersion components with increasing cycles. However, it speaks against the fact that the surface energy has no changes with increasing transfer steps. Impairment of the chemical resistance should begin on the surface, which should be seen as a change in the contact angle at the phase boundary. Since the SFE has no significant change in the polar or dispersive component, this hypothesis can be discarded.
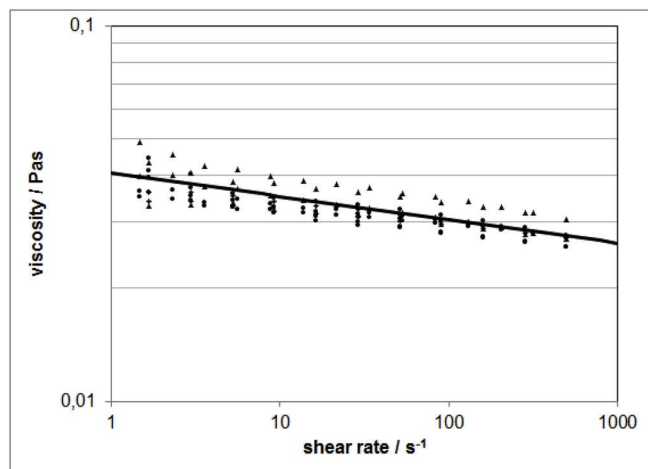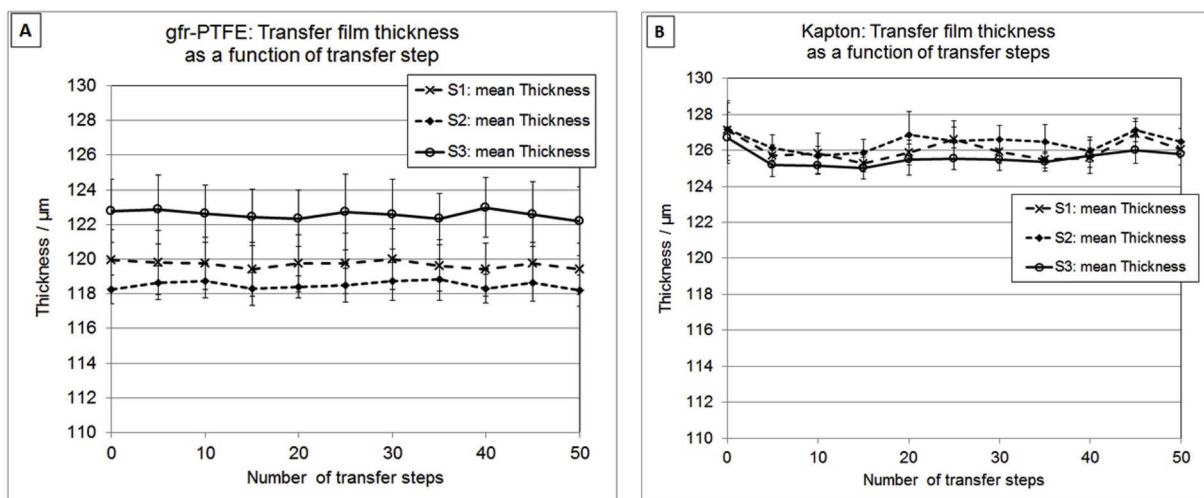
Fig. 3. Thickness of decal films as a function of the transfer step number. A) Decal film: gfr-PTFE. B) Decal film: Kapton.
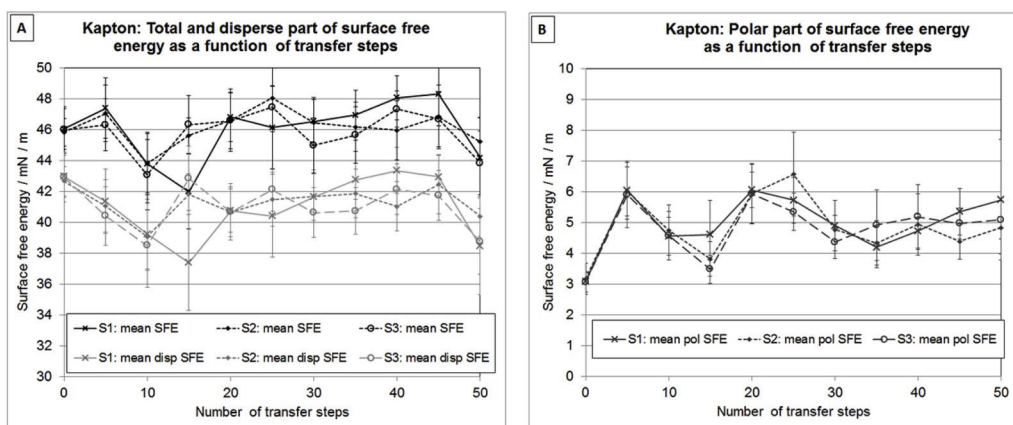

Fig. 4. Surface free energy of Kapton as a function of the transfer step number: A) Mean values of the total surface free energy and the dispersion part; B) Mean values of the polar part.
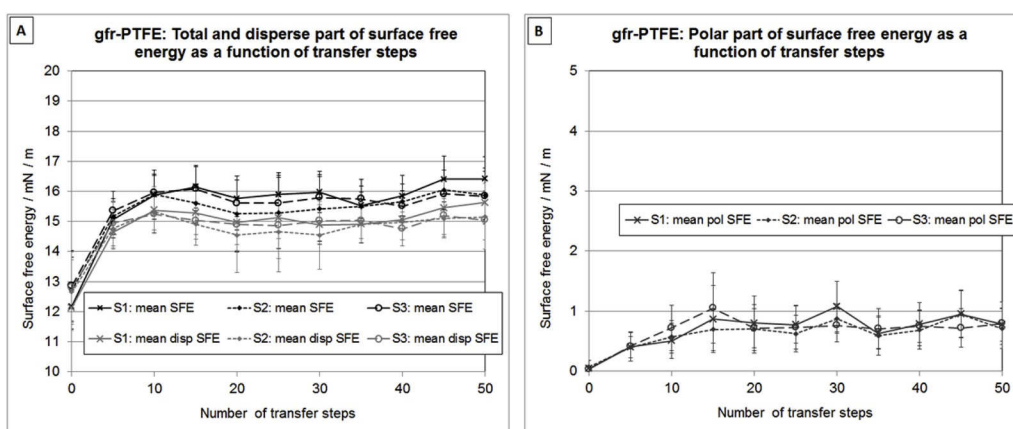

Fig. 5. Surface free energy of gfr-PTFE as a function of the transfer step number: A) Mean values of the total surface free energy and the dispersion part; B) Mean values of the polar part.

Another cause for the increasingly poor TR in the repeated use of Kapton could also indicate inhomogeneity in the dispersion. Locally varying ionomer concentrations could result in increased adhesion between ionomer and Kapton since the ionomer acts as a binder. This could lead to increased occurrence of cohesion failures in the layer after transfer. Hence, this is contrasted by the rheological data, which would reveal inhomogeneities by different courses of the flow curves. In addition, the transfer defects would also have to occur in other places, and not just in the edge areas, which also allows this hypothesis to be discarded.
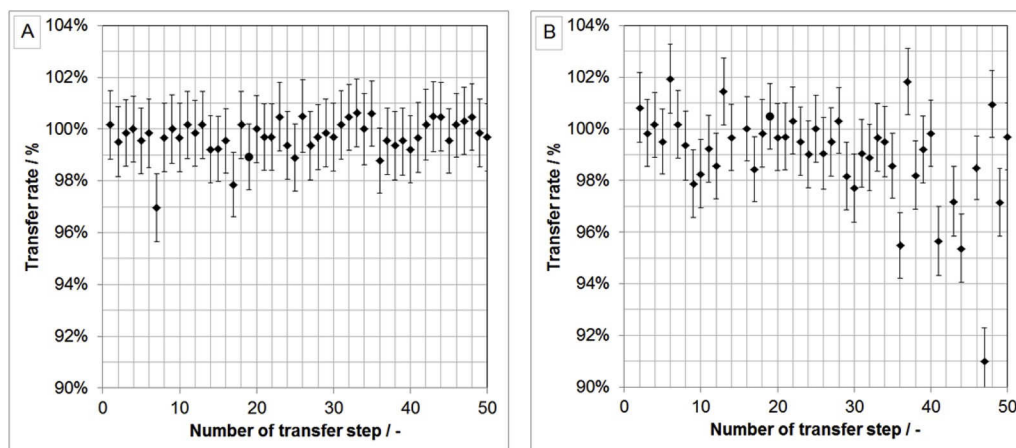
Fig. 6. Transfer rate as a function of the transfer step number: A) Decal film: gfr-PTFE, transferred basis weight (1.06 ± 0.04) mg cm^{-2}; B) Decal film: Kapton, transferred basis weight (1.04 ± 0.05) mg cm^{-2}.
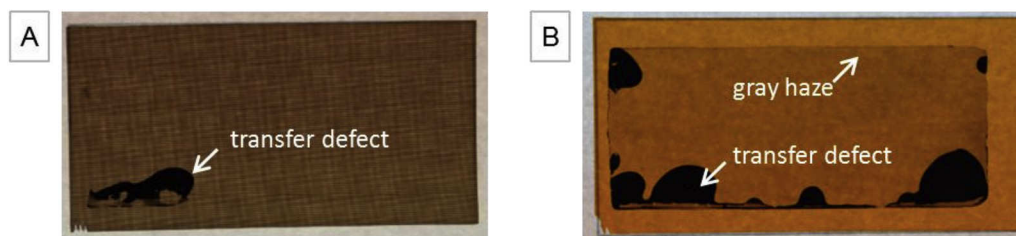

Fig. 7. Exemplary photo of decal films after the transfer process: (A) gfr-PTFE small sharply-defined areas of transfer defects. Outside of these ranges, the carbon/ Nafion layer was transferred completely (adhesion break); B) Kapton small, sharply defined areas where the transfer was incomplete. Outside of these ranges, a residual layer (gray haze) indicates a break in cohesion during the transfer process.

Since the first 30 cycles were without affecting the TR, the transfer parameters seem to be well chosen and in the case of gfr-PTFE this is confirmed by the experimental series. Nevertheless, in the case of Kapton, further adaptation of the transfer parameters could result in improved TR over the 50 cycles, for example, by increasing the temperature or adjusting the pressure.

The substrate should be selected according to the requirement and dispersion composition. Since the gfr-PTFE has enabled reliable transfer over the entire 50 cycles under constant conditions, this represents the more suitable material. Kapton can also be reliably used for up to 30 cycles. If gfr-PTFE is unsuitable in a process, for example because of poor wettability properties, Kapton is a suitable material with some limitations. Whether a higher reusability under other conditions is possible, was not further investigated in this work, but is advisable depending on the application for future work.

4. Conclusions

This study focuses on the reusability of the decal substrates used for the CCM manufacturing for PEM electrolyzers or fuel cells. A 50-time reuse of gfr-PTFE can be shown under the requirement of a reliable transfer rate in the hot pressing process. Due to the decreasing transfer rate by the use of Kapton, a reliable use cannot be made more than 30 times under the given conditions. If the reuse of the decal substrate is desired in continuous CCM production, where the catalyst dispersion is intermittently applied to the substrate and does not need to be die-cut, the use of gfr-PTFE is recommended because of substantially lower transfer errors and better reusability. Nevertheless, failures also arose in the hot pressing process onto the membrane in the case of gfr-PTFE. The observed effects of small, sharply defined areas on gfr-PTFE only appeared in some cases, but for large area coatings, such effects are undesirable and degrade the yield.

In this study, the cause of these effects could not be clarified. To guarantee process stability and the production of homogeneous electrodes, it is important to understand the reason why in some cases cohesive fractures may occur in the layer. For this purpose, the cohesion mechanisms must be elucidated and the questions must be answered, as well as how the layers adhere to the substrate, how the molecular interactions are built up and how they can be affected by the hot pressing process. An adapted hot pressing process may lead to better results when using Kapton.

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