

Thermal decomposition of PVB (polyvinyl butyral) binder in the matrix and electrolyte of molten carbonate fuel cells

J.J. Seo ^a, S.T. Kuk ^b, K. Kim ^{b,*}

^a Korea Basic Science Institute Seoul Branch, 126-16 Anam-dong, Sungbuk-Ku, Seoul 136-701, South Korea

^b Department of Chemistry, Korea University, 1 Anam-dong, Sungbuk-Ku, Seoul 136-701, South Korea

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Abstract

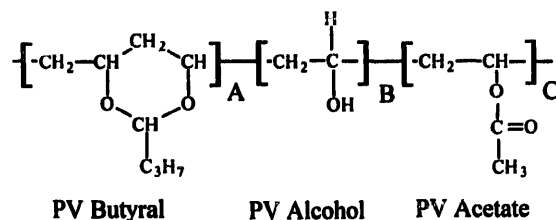
In order to determine the burnt-out condition of polyvinyl butyral as a binder in the fuel cell, thermal gravimetric analysis, gas chromatography and gas chromatography/mass spectrometry are used to analyse decomposed products during the thermal decomposition process in the matrix-green sheet and electrolyte-green sheet. Most of thermal degradation takes place under 400 °C, but degradation-resistant structures still remain up to 700 °C. Adding water vapour to the atmosphere gas could be one method to promote thermal degradation. Butyraldehyde and butene peaks among the released gases show characteristic decomposition behaviour. Thus, the butyraldehyde and butene peaks can be used as an index to check the extent of decomposition in the thermal decomposition process. © 1997 Elsevier Science S.A.

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1. Introduction

Polyvinyl butyral (PVB) is employed in various industrial and commercial applications. PVB is widely used as a binder in ceramic processing. It is prepared from aldehyde and polyvinyl alcohols. The relative proportions of hydroxy groups, acetate groups and acetal groups are controlled by the conditions of the acetal reaction. The fractions of the acetate groups are less than 2 wt.% ($C \leq 2$ wt%), and alcohol groups are up to 20 wt.% ($B \leq 20$ wt%). The hydroxyl and acetate groups act as promoters of polymer adhesives in the ceramic surface.

A molten carbonate fuel cell (MCFC) is composed of an electrode, electrolyte, matrix, and separator plate. A typical fabrication process for the electrode and the matrix involves tape-casting an appropriate mixture of metallic substrate, binder, and various additives. PVB is used as a binder in this processing and the structure is as follows:



* Corresponding author. Fax: 82 2 928 7387; Tel.: 82 2 920 147.

In the tape-casting process or ceramic fabrication process, it is important to control the burn-out of the organic additives, to minimize a residual carbon that may inhibit the sintering. The electrodes of the fuel cell must maintain a stable porous structure during the sintering process. The fuel cell is operated at 650 °C. Therefore, the thermal decomposition and elimination of the binder are important factors to operate the fuel cell smoothly.

The decomposed reaction mechanism of PVB is not simple because PVB is a copolymer and the decomposed products are very complicated [1]. Bakht [2] studied the decomposition of PVB in a vacuum system. It was reported that butyraldehyde was produced by both a free-radical mechanism and an intra-molecular elimination reaction, and that water arose from dehydration of the vinyl alcohol unit. The burn-out of PVB from green bodies of various oxide ceramics was studied by Maisa et al. [3]. The decomposition of the polymer to release butyraldehyde, in air or in argon, was enhanced by the presence of oxide powders. They proposed a cyclic elimination mechanism to release aldehyde and unsaturated end-groups. The influence of different metal powders on the thermal decomposition of PVF (polyvinyl formal) was studied by thermal gravimetric analysis (TGA) [4]. It was found that metal powders catalyze the degradation process and accelerate the weight loss of the PVF. Yamanaka et al. [5] studied thermal decomposition of PVB, PVB/PLZT,

($\text{Pb}_{0.88}\text{La}_{0.12}(\text{Zr}_{0.70}\text{Ti}_{0.3})_{0.97}\text{O}_3$ and PMN ($\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$) dielectric powder composite using a pyrolysis gas chromatography method.

In hydrogen-containing water vapour, Wall and Shon [6,7] studied the experimental and mathematical investigation of the removal of carbonaceous residue deposited on the ceramic substrate in the fabrication of multilayer ceramic modules. Carbonaceous residue reacts with water vapour to form carbon monoxide and hydrogen gas. Their report was concerned specifically with the formation of carbonaceous residue and the intrinsic kinetics of its subsequent removal in a mixture of water vapour with hydrogen.

PVB was completely burnt out in the electrodes because nickel-green sheet was sintered at 850 °C before operating. By contrast, PVB in the matrix-green sheet and electrolyte-green sheet is thermally decomposed during the operating process of the fuel cell. The operating temperature of the fuel cell is 650 °C, and the thermal decomposition of PVB in the fuel cell is different from that in PVB alone. The thermal decomposition temperature and the decomposition rate of PVB usually depend on the composition of the metal mixtures with PVB.

Previously, we reported [8] the thermal decomposition of pure PVB and nickel-green sheet in both air and air-containing water vapour. In the present study, the thermal decomposition process of PVB in matrix-green sheet and electrolyte-green sheet are investigated in air, and air-containing water vapour using TGA, gas chromatography (GC) and gas chromatography/mass spectrometer (GC/MS) for reducing the amount of residual carbonaceous material and finding the appropriate operating condition of the fuel cell.

2. Experimental

2.1. Materials

The PVB used in this study was Butvar B-98 (Monsanto). The electrolyte-green sheet was $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ (62/38 m/o) with 14 wt.% PVB and the matrix-green sheet was $\gamma\text{-LiAlO}_2$ with 20 wt.% PVB. Green sheets were made by the tape-casting method.

2.2. Instrumentation

TGA (Stanton Redcroft TG1000) was used to monitor the weight changes at a heating rate of 10 °C/min. To make air-containing water vapour, a supporting apparatus was produced [8]. The feed gas was generated by bubbling air gas through de-ionized water kept at 50 °C and this apparatus was connected to the furnace. The decomposed gases through the furnace were collected by a gas-tight syringe at the hot stage and immediately analysed by GC and GC/MS at every 100 °C. The gas flow-rate was 100 ml/min and the heating rate of the furnace was 2 °C/min.

GC was carried out with a HP 5890 (Hewlett-Packard) instrument equipped with a flame ionized detector, a 12 m \times 0.32 mm Polaplot-Q (CHROMPACK) column with a 20 μm film thickness and a HP 3396A integrator. The injection port and detector temperature were 200 and 230 °C, respectively. The oven temperature was programmed with a initial hold for 2 min at 30 °C, followed by an increase at 10 °C/min to 230 °C, and then with a hold for 10 min. The nitrogen carrier gas flow was 1 ml/min and the nitrogen make-up gas was set at 30 ml/min.

MS measurements were made with an HP 5988 (Hewlett-Packard) mass spectrometer interfaced to a HP 5890 GC unit. All column conditions were the same as the GC conditions except for carrier gas. The mass-operating conditions were as follows: source temperature: 200 °C; electron energy: 70 eV; helium carrier gas-flow: 0.9 ml/min.

All of the relative comparisons were made with the GC result. The GC/MS data were used only for the identification of GC peaks.

3. Results and discussion

3.1. Thermal analysis

According to TGA, PVB decomposes in several stages. Fig. 1 shows the various TGA curves for the individual MCFC components. The pure PVB is completely decomposed around 500 °C. In the presence of the various metal components, the decomposition temperature of the green sheets are lowered to around 200 °C. The decomposition temperature of both the matrix-green sheet and the electrolyte-green sheet in air conditions is shifted to a lower value (Fig. 1(C), (D)). This means that the metal components promote the decomposition reaction to produce butyraldehyde, which is the main decomposition product. The TGA curve of the nickel-green sheet in air displays a decomposition tendency that is similar to the other green sheet, but the weight percentage is increased at above 400 °C due to the oxidation of nickel.

Most of the decomposition process of the matrix-green sheet and the electrolyte-green sheet is completed under 300 °C. Compared with the decomposition of pure PVB, the decomposition rate of green sheet is accelerated. In the fuel-cell setting, nickel-green sheet is sintered before operating and the decomposable binder components remain in the matrix and electrolyte. Therefore, it is safely concluded that PVB binder is almost burnt out below 400 °C which is the gas-changing temperature of the MCFC.

3.2. Gas chromatographic analysis

To examine the general behaviour of thermal decomposition of two types of green sheet under air and air-containing water vapour, the sums of the decomposed gases were plotted. Fig. 2 shows the area sums of thermally decomposed gases,

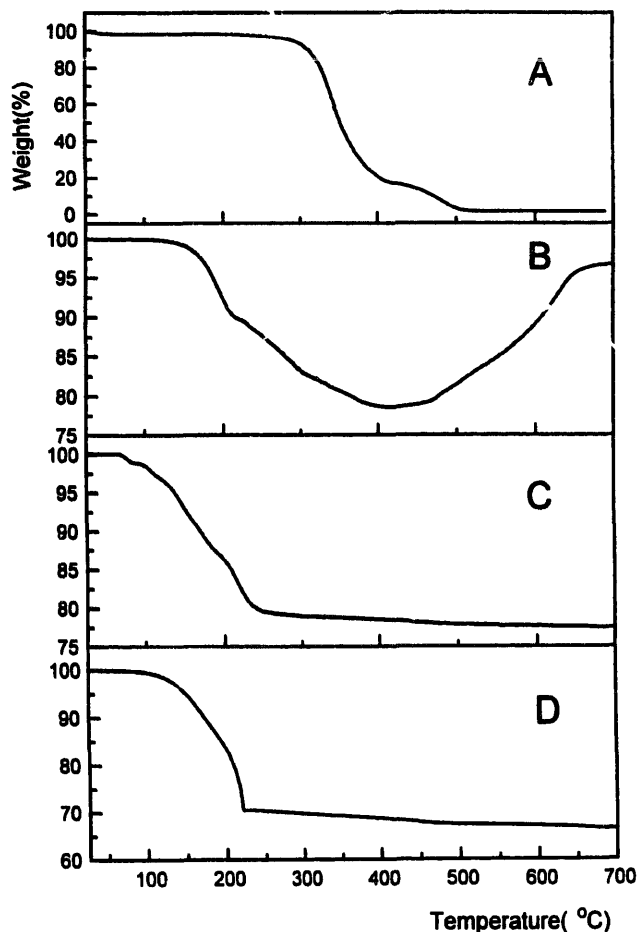


Fig. 1. TGA plot of PVB decomposition in air at 10 °C/min. (A) PVB 100%; (B) nickel-green sheet (PVB 20 wt.%); (C) matrix-green sheet (PVB 20 wt.%), and (D) electrolyte-green sheet (PVB 14 wt.%).

which were analysed by GC. All data were normalized. Matrix-green sheet is rapidly decomposed at around 200 °C in air-containing water vapour and at 300 °C in pure air. The electrolyte-green sheet displays, almost the same maximum

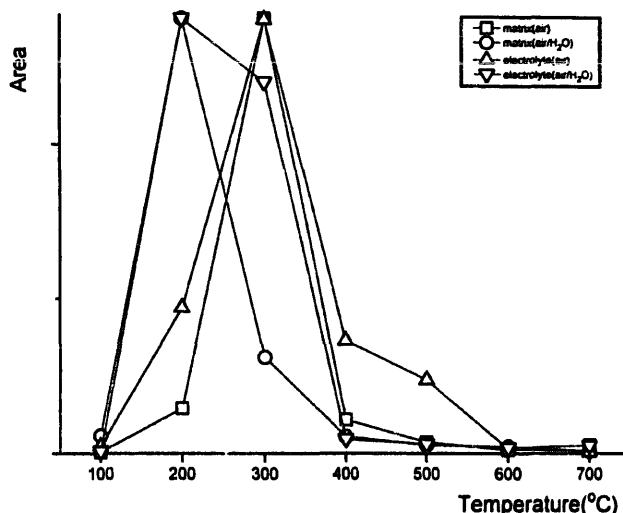


Fig. 2. Total area vs. temperature plot of GC graphs. \star air/H₂O means the air-containing water vapour.

decomposition temperature, but the decomposition rate of electrolyte-green sheet is slower than that of matrix-green sheet. The matrix-green sheet is almost burnt out at 200 °C, but the decomposition of electrolyte-green sheet still continues even above 400 °C. TGA data also show that the decomposition slope of matrix-green sheet is less than that of electrolyte-green sheet in the 200 to 500 °C range. Both green sheets display a lower decomposition temperature in air-containing water vapour than in pure air. Therefore, the binder decomposed more rapidly when water vapour was added to the gas.

Fig. 3 shows the maximum decomposition temperatures of the individual MCFC components in the two gas conditions. The data indicate that the catalytic effect of the various metal components occurs during thermal decomposition of the PVB. All the green sheets reduce the temperature of maximum decomposition with respect to pure PVB. The latter

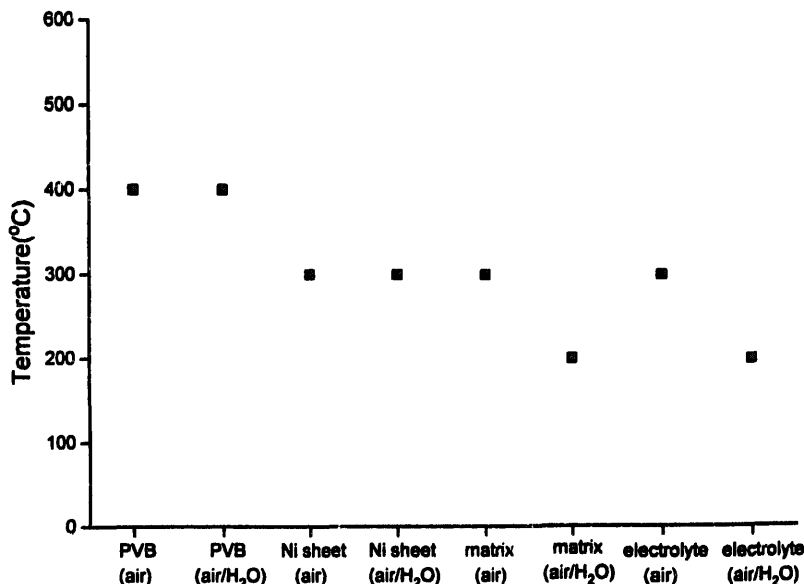


Fig. 3. Maximum decomposition temperature for individual fuel cell components in air and air-containing water vapour.

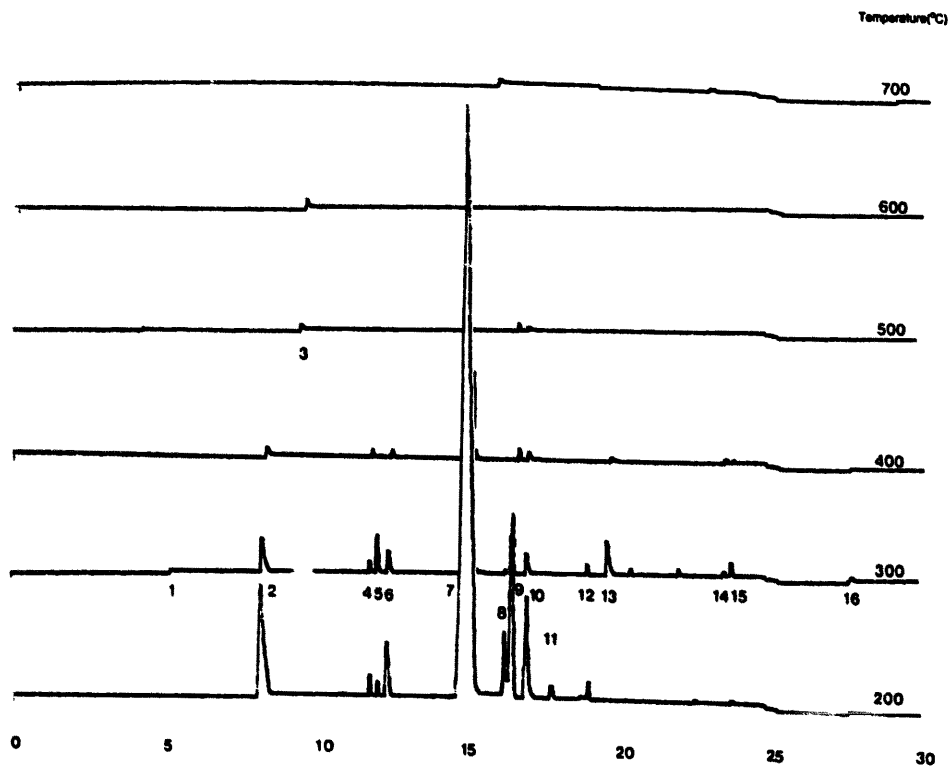


Fig. 4. Thermal decomposed GC graphs of matrix-green sheet in air-containing water vapour: (1) propene, propane; (2) acetal; (3) butene; (4) propenal; (5) propanal; (6) propanone; (7) butanal; (8) butenal; (9) benzene; (10) butanol; (11) C_5H_8O 12,3-penten-2-one; (13) butanoic acid; (14) phenol; (15) benzaldehyde, and (16) 1-phenylethanone.

shows a maximum at around 400 °C in both conditions. The maximum decomposition points for various green sheets are around 300 °C. In the presence of each metal component, the maximum decomposition points are shifted to a lower temperature and this result coincides with the TGA data. The decomposition begins early in air that contains water vapour so that thermal decomposition of PVB is completed earlier than in pure air. It is suggested that organic compounds such as carbonaceous residue react with oxygen in the water vapour.

For the individual fuel cell components, the major decomposed gases (analysed by GC/MS) are very similar but the relative amounts of produced gases are different from one another. The chromatogram of the matrix-green sheet is simpler than that of the electrolyte-green sheet. The major produced gases are similar to each other, but the minor compounds are quite different. Generally, the major decomposed gases are light hydrocarbons, alcohols, aldehydes and ketones where carbon numbers are less than C_8 . This result is similar to that of the previous study on the thermal decomposition of PVB and nickel-green sheet [8]. The major produced gases are nearly the same in pure air and air-containing water vapour, but the decomposition temperature displays a large difference, as shown in Fig. 3.

Fig. 4 shows the GC graphs of decomposed gases at different temperatures during the thermal decomposition of matrix-green sheet in air-containing water vapour. Most of the decomposition occurs below 300 °C and GC peaks almost disappear above 500 °C, except for butene. The decomposed

compounds of matrix-green sheet are alkenes, aldehydes, ketones, carboxylic acids, phenols, and benzaldehydes. In all cases, the major produced compound is butyraldehyde, which is formed during breakage of the carbon backbone.

The minor produced gases of electrolyte-green sheet are somewhat different from those of other components (Fig. 5). The major products are almost the same within 17 min of retention time, but the minor components of later-eluting peaks are totally different from the gases of matrix-green sheet and nickel-green sheet. Hence, it is noted that relatively large and aromatic compounds such as 2,4-hexadienal and methylbenzaldehyde appear after 15 min, which is the retention time of butyraldehyde. Electrolyte-green sheet may have different thermal decomposition behaviours, because electrolyte-green sheet has many carbonate ions which possibly act as another carbon source.

The relative area changes of butyraldehyde at different temperatures are shown in Fig. 6 for matrix-green sheet and electrolyte-green sheet. The relative area plots of butyraldehyde are similar to the total area plot. Butyraldehyde is a main decomposed product because the fraction of butyral groups are up to 80 wt.% in PVB polymer. Therefore, the butyraldehyde peak indicates indirectly the extent of thermal decomposition. As discussed earlier, the decomposition of green sheet starts at lower temperatures in air that contains water vapour. The electrolyte-green sheet decomposes more slowly than the matrix-green sheet.

Figs. 7 and 8 show relative quantity changes of major produced gases against temperature. In each plot, the x-axis is

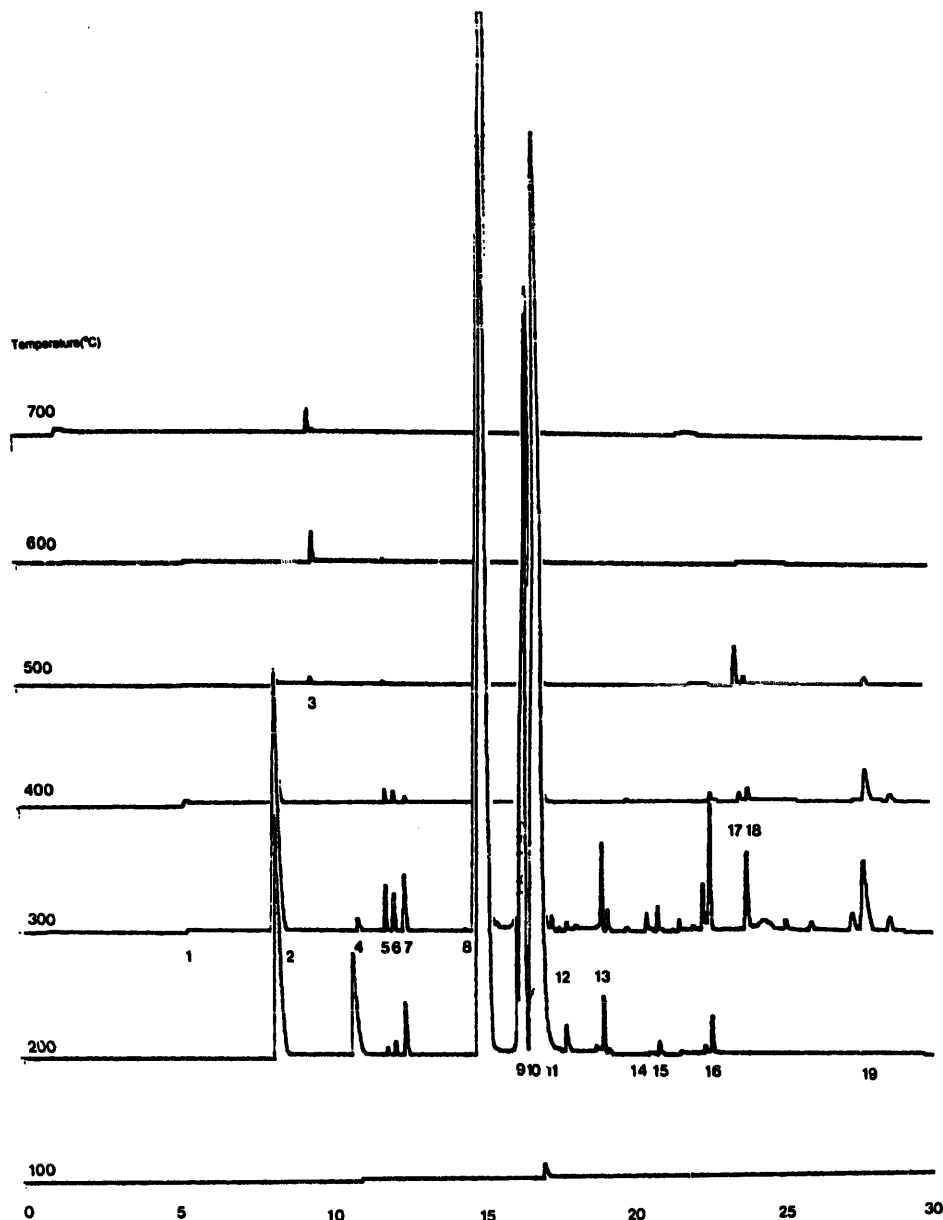


Fig. 5. Thermal decomposed GC graphs of electrolyte-green sheet in air-containing water vapour: (1) propene; (2) acetal; (3) butene; (4) ethanol; (5) propenal; (6) propanal; (7) propanone; (8) butanal; (9) butenal; (10) benzene; (11) butanol; (12) C_5H_8O ; (13) 3-penten-2-one; (14) butanoic acid; (15) methyl pentanal; (16) 2,4-hexadienal; (17) phenol; (18) benzaldehyde, and (19) methyl benzaldehyde.

the decomposition temperature and the y-axis is the area of the GC peaks. Here, the change of the produced gases of the green-sheet is known from the relative area distribution of temperature. Fig. 7 shows the area distribution of propene, butene, butanoic acid and phenylethanone in air and air-containing water vapour. The earlier-eluting light compounds of matrix-green sheet (such as propene) produced a lower temperature than electrolyte-green sheet. The amount of produced gas in air was more than that in air-containing water vapour. The acetaldehyde peak displays similar behaviour. In contrast with other GC peaks, a butene peak is detected at high temperature and shows a maximum at around 500 °C. Most of the GC peaks almost disappear even under the melting point of the electrolyte-green sheet, 500 °C. Therefore,

measurement of the butene peak in high temperature allows determination of the extent of the decomposition process.

A butene peak is not detected at any temperature in the decomposition of pure PVB [8]. Thus, the appearance of a butene peak suggests that the decomposition process of PVB in various metal components is different from that in pure PVB. This means that butene is a possible product due to the decomposition of the degradation-resistant cyclic and cross-linked structure that is formed at lower temperatures during the side-group elimination and chain-scission reaction. Therefore, it is necessary to find proper conditions to decrease the butene peak by as much as possible to lower decomposition temperatures. The addition of water vapour could be one of the possible methods to decrease the butene peak.

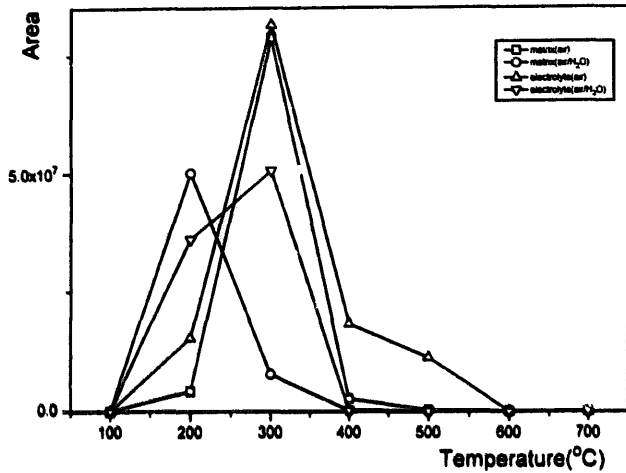


Fig. 6. Relative area change of butyraldehyde at different temperatures.

Butanoic acid and phenylethanone are released in only small amounts during the thermal decomposition of electrolyte-green sheet, but in greater amounts with the matrix-green sheet.

Ethanol and butanol are detected more in the decomposition of the electrolyte-green sheet than in that of the matrix-green sheet (Fig. 8). The same holds for benzaldehyde and methylbenzaldehyde. Therefore, the decomposition behaviour of the electrolyte-green sheet differs from that of other green sheets because it contains a carbonate fraction. The decomposition of the electrolyte-green sheet is influenced by produced CO_2 during the thermal decomposition process. At a higher temperature, the amount of produced cyclic compounds in air that contains water vapour is less than that produced in pure air. The reason is that oxygen promotes decomposition of the PVB in air that contains water vapour.

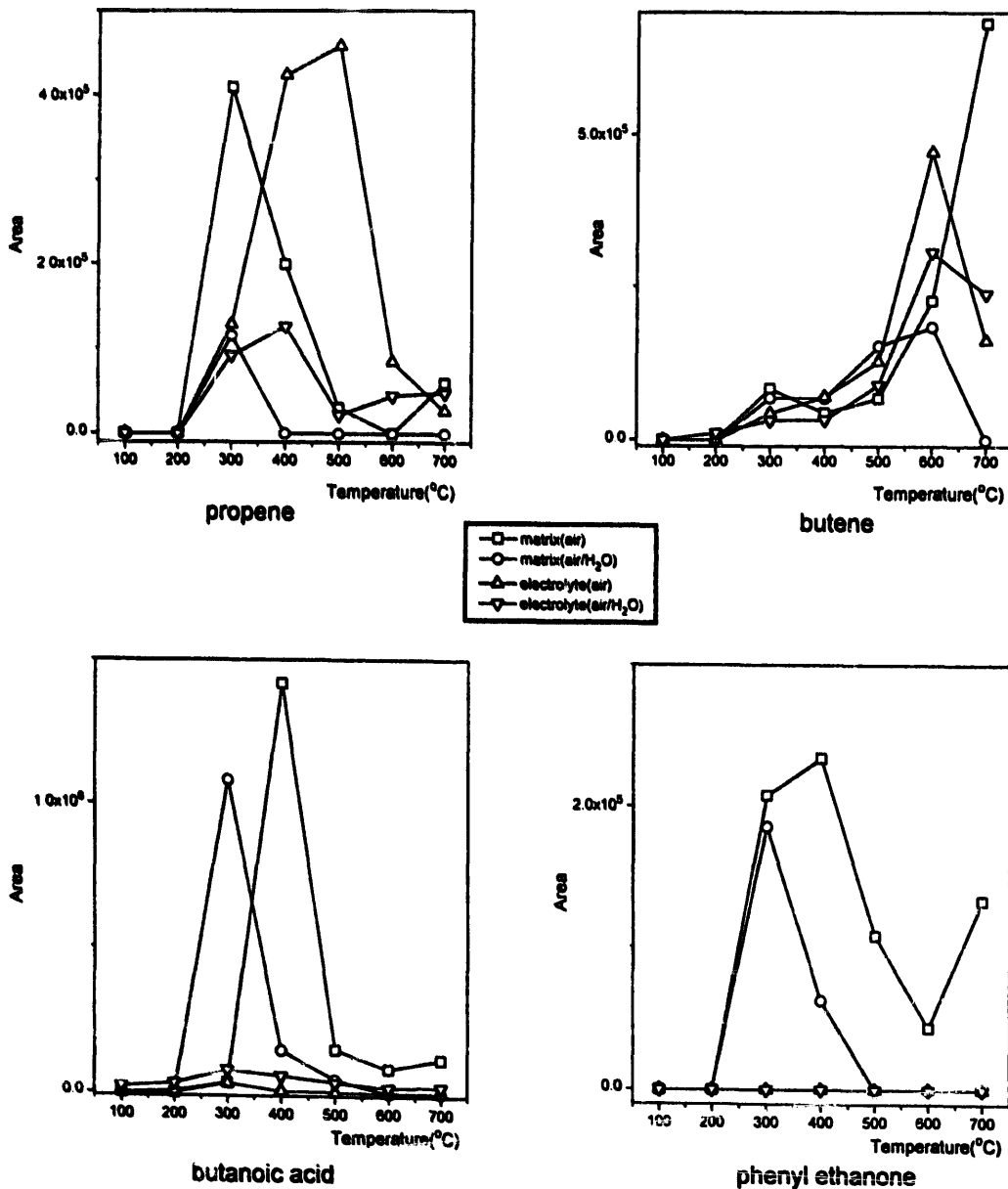


Fig. 7. Relative amount of various produced gases on the thermal decomposition gas chromatogram vs. temperature.

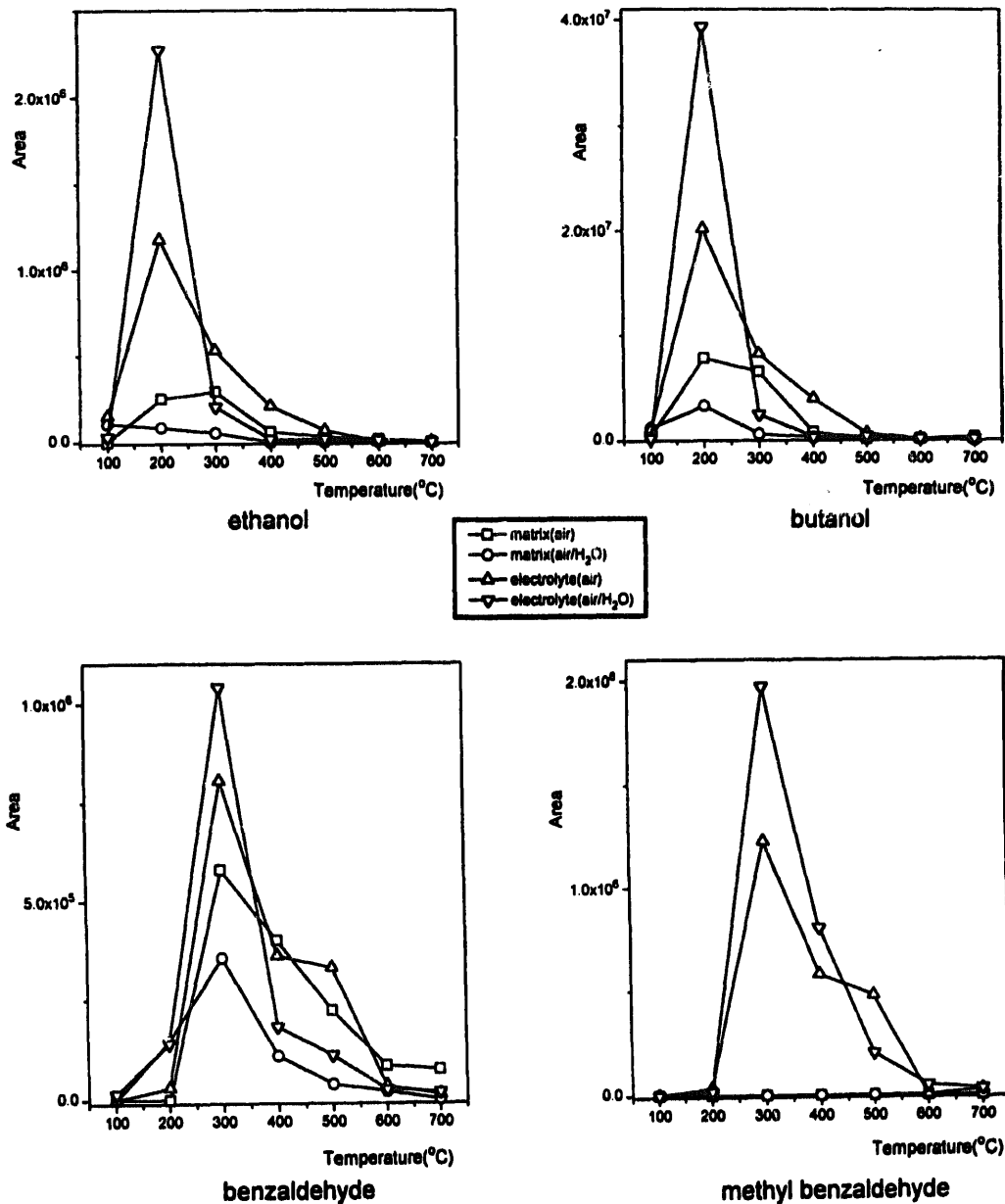


Fig. 8. Relative amount of various produced gases on the thermal decomposition gas chromatogram vs. temperature.

Consequently, the degradation process is completed earlier than in pure air.

4. Conclusions

The thermal decomposition temperature of PVB is influenced by the metallic substrate. Most of the binder in electrolyte-green sheet and matrix-green sheet is burnt out at around 400 °C in fuel cell operation. Therefore, oxygen is supplied until at least 400 °C because thermal degradation is initially accelerated in air due to oxidative mechanisms.

When water vapour is added to the atmosphere gas condition, the decomposition temperatures are shifted to lower values. To complete the thermal degradation reaction of the binder under the melting point of electrolyte-green sheet, it

is necessary to lower the decomposition temperature. The finding of an appropriate catalyst that does not effect the specific character of the individual fuel cell components or adding water vapour can be methods to overcome this problem.

The relative change of the butyraldehyde peak indirectly indicates the decomposition process because butyraldehyde is the main decomposition product of PVB polymer. Also, the butene peak shows the extent of termination in higher temperatures where other peaks almost disappear. Hence, the butyraldehyde and butene peaks can be used as an index to check the extent of decomposition.

Acknowledgements

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