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Determination of Optimum Production Conditions of Casting Slurry in the Manufacture of Molten Carbonate Fuel Cell Electrodes with the Tape Casting Technique

Gülay Özkan[b*], Selim Gemici[b], Erdi Başarır[b], Goksel Özkan[a]

[a]Department of Chemical Engineering, Gazi University, 06570 Maltepe, Ankara, Turkey
[b]Department of Chemical Engineering, Ankara University, 06100 Tandoğan, Ankara, Turkey
gozkan@eng.ankara.edu.tr

In this study, Ni anode and $LiAlO_2$ electrolyte green sheets were manufactured for MCFC system. Experimental scale production of green sheets was carried out by using tape casting technique. The method of casting slurry, which is the first stage of preparation, has a direct impact on the final product. Therefore, cast slurries with different ratios of a solvent, a binder, a dispersant, plasticizer loading to the organic compounds were prepared to produce green sheets with the technique of tape casting in order to investigate the viscosity, shear stress, thixotropy and flow characteristics. After sheets were dried, physical properties (mechanical tests) were determined. Mixing method (balling mill and mechanical stirrer) and mixing duration of slurry, mixing weight ratio of binder, solvent, plasticizer, dispersant, Li/K carbonate, Ni, and $LiAlO_2$ powder in the slurry was examined.

1. Introduction

Molten Carbonate Fuel Cells (MCFC) are called according to its electrolyte as well as other fuel cells. MCFC has high energy conversion efficiency and operates between 650 - 700 °C. Usually, it comes at the beginning of the systems used in the local and regional level to high energy needs. In recent years, fuel cell electrode and electrolyte materials in the production of tape casting technique are known to find the area of intensive use. Nowadays tape casting technique is especially widely used in the production of plate and coating processes such as thin ceramic coating, polymeric coating, porous coating and the metal or alloy coating. Especially, this technique is used in the preparation of membrane, electrodes and electrolyte matrix of the polymeric membrane fuel cell (PEMFC) (Antolini, 2011), molten carbonate (MCFC) (Antolini, 1996) and solid oxide (SOFC) fuel cell (Özkan et al., 2015) and further discussion in (Özkan et al., 2016).

In this study, Ni anode and $LiAlO_2$ electrolyte green sheets were manufactured for MCFC system. Experimental scale production of green sheets was carried out by using tape casting technique. The method of casting slurry, which is the first stage of preparation, has a direct impact on the final product. Therefore, cast slurries with different ratios of a solvent, a binder, a dispersant, plasticizer loading to the organic compounds were prepared to produce green sheets with the technique of tape casting in order to investigate the viscosity, shear stress, thixotropy and flow characteristics. After sheets were dried, physical properties (mechanical tests) were determined. Mixing method (balling mill and mechanical stirrer) and mixing duration of slurry, mixing weight ratio of binder, solvent, plasticizer, dispersant, Li/K carbonate, Ni and $LiAlO_2$ powder in the slurry and rheological characterization of slurries were examined.

The optimum amount of cast slurries with different ratios of a solvent, a binder, a dispersant, plasticizer loading to the organic compounds was selected. The purpose of this study was to investigate the effect of green tensile strength because of good indicator of green tape homogeneity, which will also affect the sintering behavior. The ultimate tensile stress is important for handling. High strain to failure in the tape is necessary for successful removal of tapes from the carrier substrate and subsequent handling. Tape casting is

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a powerful method for manufacture of nickel green sheet which is sintered at high temperature for example 800 °C.

2. Materials and Methods

Anode material was prepared by milling nickel, polyethylene glycol, polyvinylbutyral, glycerol in an organic medium (ethanol). Sintering process was carried out at 800 °C.

The matrices for the molten carbonate fuel cell were manufactured by tape casting method of a slurry that consisted of an organic solvent (ethanol), binder (polyvinyl butyral), plasticizer (polyethylene glycol), dispersant (glycerol) and lithium aluminate, potassium carbonate, lithium carbonate.

Ethanol was used as a solvent in the slurry when mixing period and method was changed. Slurry had been mixed in the ball-milling before it was mixed with mechanical stirrer. The ratio of the nickel powder that is 32 - 53 % was used in the anode slurry. The best weight ratio is 32 % for nickel powder. In addition, 13 - 52 % by weight of ethanol was used in the anode slurry. The best weight ratio is 41 % for the solvent (ethanol). 1,5 PVB (Polyvinyl butyral) / PEG (Polyethylene glycol) (w/w) was optimized for anode.

22 - 32.3 % by weight of lithium aluminate ($LiAlO_2$) powder was used in the electrolyte slurry. The best weight ratio is 32 % for lithium aluminate powder. An amount varying between 23 - 52.3 % by weight of ethanol was used in the electrolyte slurry. The best weight ratio is 45.7 % for the solvent and 4.4 : 3.8 wt % for K/Li carbonate, 6.2 wt % for PVG, 7.1 wt % for PEG and 0.5 wt % for glycerol was used in the electrolyte mixture.

Table 1: Material list

	Binder	Solvent	Powde	Dispersant	Plasticize
Anode	PVB	Ethanol	Ni	Glycerol	PEG
Electrolyte	PVB	Ethanol	$LiAlO_2$	Glycerol	PEG

Anode materials are given in Table 1.The process of tape casting was performed on nickel powder that shows in Figure 1.

- ✓ 20 g Ni powder added to the milling.
- ✓ 15.8 g Ethanol was used for nickel powder in the milling
- ✓ This slurry was ball milled for 4 h in order to separate nickel particles and to break up weak agglomerates.
- ✓ Then 1 g binder PVB ,0.5 g PEG and 0.5 g glycerol added to the mill.
- ✓ 15 pieces ball used in the mill and slurry was milled for 48 h at 47 rpm.
- ✓ The slurry was then cast on the glass surface and dr blade was used to prepare green sheet.
- ✓ Green sheet was sintered at 800 °C with the CO_2 and O_2 in the furnace

Also, electrolyte materials are given in Table 1.The process of tape casting was performed on lithium aluminate powder that shows in Figure 2

- ✓ 22 g $LiAlO_2$ powder added to the milling.
- ✓ 46 g Ethanol was used for $LiAlO_2$ powder in the milling
- ✓ 5 g $LiCO_3$ and 44 g K_2CO_3 added to the mill.
- ✓ This slurry was ball milled for 4 h in order to separate $LiAlO_2$ particles and to break up weak agglomerates.
- ✓ Then 7 g binder PVB, 8 g PEG and 1 g glycerol added to the mill.
- ✓ 15 pieces ball used in the mill and slurry was milled for 48 h at 47 rpm.
- ✓ The slurry was then cast on the glass surface and dr blade was used to prepare green sheet.
- ✓ Green sheet was sintered at 800 °C with the CO_2 and O_2 in the furnace

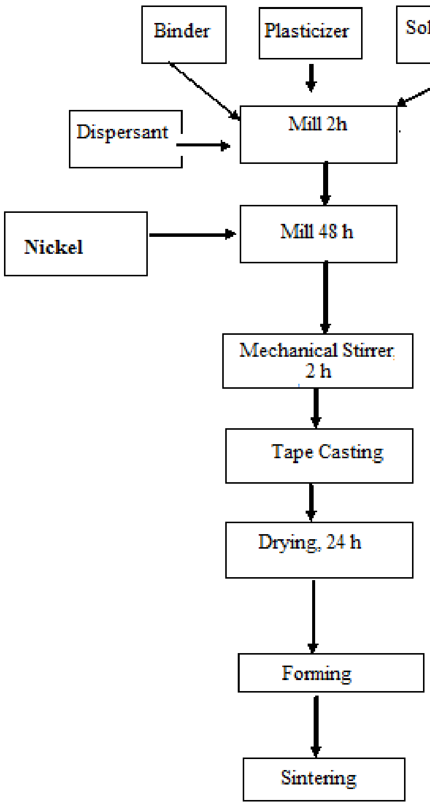

Figure 1: Experimental procedure for anode

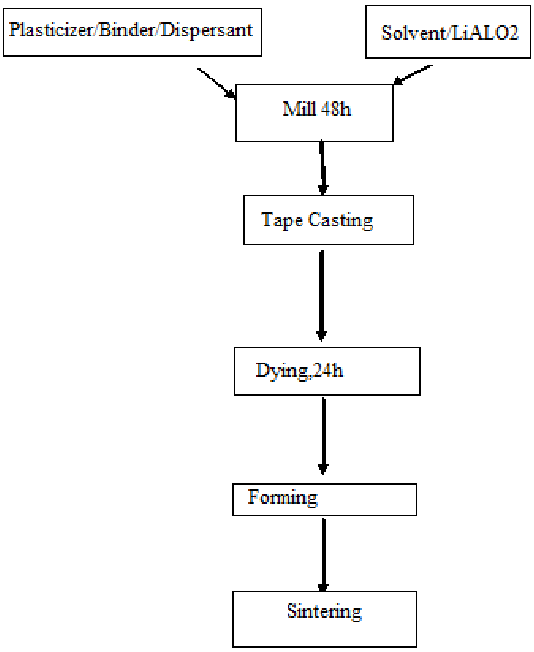

Figure 2: Experimental procedure for electrolyte

3. Result and Discussion

3.1 Tensile test

Tensile strength, displacement, stress, strain and thickness of the green sheet were analyzed by performing tensile test. Green sheet samples were pulled off by test device with 1 mm/min. Thickness was 0.4 mm in experiment 1 on the other hand thickness of the green sheet was increased in experiment 2. Maximum displacement of the sample was decreased from 4,421 mm to 3,877 mm and tensile strength was decreased. Maximum stress was decreased from 4.4244 N/mm^2 to 0.819 N/mm^2 on the other hand maximum strains was increased from 6, 3 % to 12, and 9 %. The tensile strength and strain to failure off green sheets were measured. As can be seen in Table 2, the strength of the green sheet decreased and amount of PVB was decreased in the mixture totally.

Table 2: Physical Properties of Anode

	Experiment No 1	Experiment No 2
PVB (g)	4.8 (15 %)	1.5 (3.9 %)
PEG (g)	3.2 (10 %)	0.5 (1.3 %)
Ethanol (g)	13 (41 %)	15.8 (41 %)
Glycerol (g)	0.25 (0.8 %)	0.5 (1.3%)
Ni (g)	10 (32 %)	20 (52 %)
Maximum Strength (N)	53.0938	49.3156
Maximum Displacement (mm)	4.421	3.877
Maximum Stress (N/mm^2)	4.424	0.819
Maximum Strain (%)	6.315	12.923
Thickness (mm)	0.4	1.4
Width × Length (mm)	30 × 70	43 × 30
Tensile Strength/ (Width × Length) (N/mm^2)	0.025	0.038

Obviously, the binder to plasticizer ratio plays an important role in mechanical properties of green sheet. In the range less than 50 wt % PVB (50 : 50 PVB:PEG (wt/wt)), the green sheet had low strength and high flexibility because of insufficient binder among the nickel particles. On the other hand, the green sheet with PVB content than 50 wt % had high strength and stiffness due to insufficient plasticizer. Plasticizer can reduce the molecular chain length of PVB by breaking the chain and decrease the Van der Waals forces between large binder molecules.
According to Table 3, $LiAlO_2$ percentage was reduced (Experiment 4), it was observed that the tensile strength was dropped. While the dispersant ratio was rising, tensile force was also increasing. Pressure on unit surface was also increased. In case of optimum proportions of material for the dispersant or other mixture ratios, it is found to provide a homogeneous mixture. Thickness of the green sheet was 0.5 mm in experiment 3 and thickness was increased to 1 mm in Experiment 4. Maximum displacement was increased from 1.3 mm to 3.4 mm and tensile strength is decreased. Maximum stress was decreased from 1.53 N/mm^2 to 0.18 N/mm^2 and maximum strain was increased from 1.86 % to 4.25 %. Size of the green sheet was similar. Thickness of the green sheet was 1 mm in experiment 4 and thickness was increased to 1.3 mm in experiment 5. Maximum displacement was decreased from 3.4 mm to 0.305 mm and maximum strain was decreased from 4.25 % to 1.01 %. Tensile strength is increased. Maximum stress was increased from 0.187 N/mm^2 to 0.339 N/mm^2.The amounts of electrolyte material in the matrix slurries were 8.2 %, 9.4 % and 10.1. Each green matrix sheet had a thickness of 0.5 - 1.3 mm.

Table 3: Physical Properties of Electrolyte

	Experiment No 3	Experiment No 4	Experiment No 5
PVB (g)	7.1 (6.2 %)	7.1 (7.1 %)	3.5 (7.5 %)
PEG (g)	8.1 (7.1 %)	8.1 (8.1 %)	4 (8.6 %)
Ethanol (g)	52.3 (45.7 %)	52.3 (52.6 %)	23 (49.3 %)
Glycerol (g)	0.6 (0.5 %)	0.6 (0.6 %)	0.5 (1.1 %)
Li2CO3 (g)	5 (4.4 %)	5 (5 %)	2.5 (5.4 %)
K2CO3 (g)	4.4 (3.8 %)	4.4 (4.4 %)	2.2 (4.7 %)
LiAlO2 (g)	36.9(32.3 %)	21.9 (22 %)	11 (23.6 %)
Maximum Tensile Strength (N)	20.723	5.073	8.836
Maximum Displacement (mm)	1.304	3.405	0.305
Maximum Stress (N/mm^2)	1.535	0.187	0.339
Maximum Strain (%)	1.862	4.256	1.016
Thickness (mm)	0.5	1	1.3
Width × Length (mm)	27 × 70	27 × 80	20 × 30
Tensile Strength/(Width × Length) (N/mm^2)	0.011	0.0023	0.0147

3.2 Rheological characterization of slurries:
The flow curves of the anodes and electrolyte slurries obtained by measurements performed by increasing the shear rate from 0 to 100 s^{-1} for anode and 0 to 1,000 s^{-1} for electrolyte and temperature maintained constant at 25 °C were shown in Figure 3 and 4.
It is expected that the anode slurry high Ni shows the highest viscosity as well as some thixotropy which shows time dependent (Table 4). Both viscosity and thixotropy behavior decrease when solvent is added. Minimum average viscosity is reached for 32 % Ni slurry. Average viscosity of the best electrolyte (Experiment No 1) is 1.2 Pa.s. Experimental data were analyzed using different regression models. The best fitting was obtained for the Herschel–Bulkley model. As a result of researching the relation between sheer rate and sheer stress, flow behavior indexes were shown in Table 4. All the suspensions reveal a shear thinning (pseudo plastic) behavior. Shear - thinning flow behavior is described as;

- ✓ Decreasing viscosity
- ✓ Deformation in shear direction occurs disentanglement
- ✓ Agglomerates are disintegrated,
- ✓ Droplets are deformed and show the shape of ellipsoids.
- ✓ Particles are orientated in flow direction.

All of them, Shear - thinning flow behavior is appropriate for tape casting

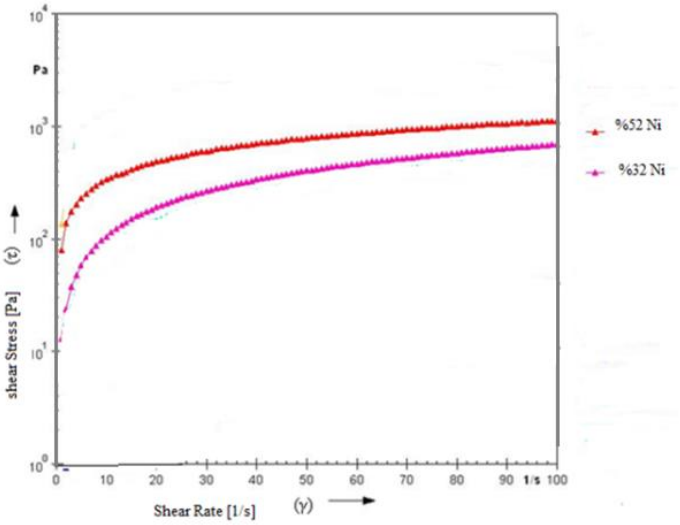

Figure 3: Flow curves for anode

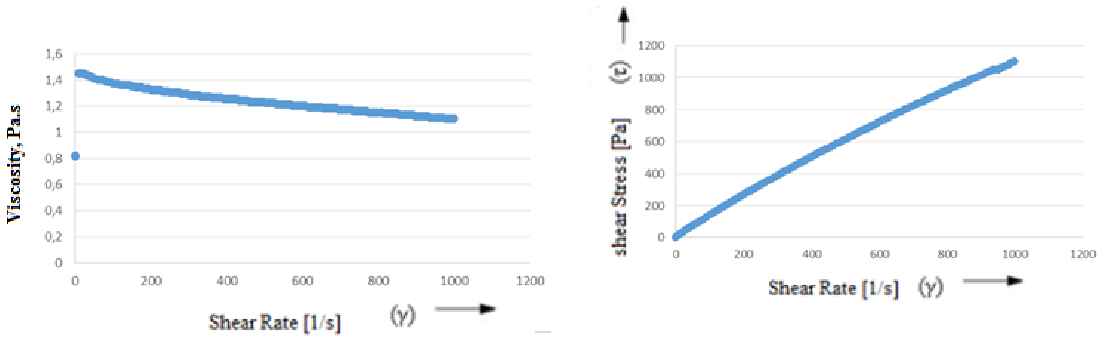

Figure 4: Flow curves for electrolyte slurries

Table 4: Thixotropy of samples

	Thixotropy (%)
52 % Anode	103,7
32 % Anode	60,78
Electrolyte	97.74

Table 5: Flow behavior index

	Flow behavior index n	Flow behavior
52 % Anode	0.49	Shear - thinning
32 % Anode	0.76	Shear - thinning
Electrolyte	0.94	Shear - thinning

4. Conclusions

This study successfully prepared Ni powder green sheet and electrolyte for sintering process. Slurry compositions of the pure $LiAlO_2$ matrix were optimized using tape casting method. The performance of unit cell with $LiAlO_2$ matrices were much improved for the mechanical tests. Electrolyte matrices were manufactured with electrolyte materials in 62 : 38 ratios for the Li_2CO_3 and K_2CO_3. Electrolyte materials were homogeneously dispersed in the matrices. $LiAlO_2$ matrices were optimized by quantification of the electrolyte materials in matrices with 32.3 % (wt) solids (Experiment No 3). Binder and plasticizer were added to the slurry after the addition of the solvent and $LiAlO_2$. It is important factor for the homogeneity of the matrix sheet. Anode electrodes were prepared with powder sintering and by tape casting methods. This had resulted in better performance for the mechanical strength test's the nickel powder increased, tensile strength was decreased. PVB ratio and thickness of the green sheet affected the mechanical properties. The best mixing got from Experimental 1.

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