PREPARATION AND CHARACTERIZATION OF POROUS NICKEL ELECTRODES FOR MOLTEN CARBONATE FUEL CELLS

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Nickel powder INCO 255 was used to prepare the electrodes. The cathode was a porous nickel plate. Pure Ni and Ni + 10% Cr were used. Aqueous slurry casting and tape casting methods using a doctor blade assembly were followed to fabricate several batches of electrodes of desired thickness. TGA analysis was employed to determine the binder and plasticizer burnt-out conditions. These electrodes were sintered in hydrogen atmosphere at 1073 K. The characteristics of the tapes such as thickness, shrinkage factor and porosity values were reported.

Keywords: Nickel electrodes, tape casting, molten carbonate fuel cells

INTRODUCTION

Molten Carbonate Fuel Cells (MCFC) are presently under development for electric utility power generation [1,2]. Porous nickel plaques with 50 to 70% total porosity and with average pore diameter in the range 4-6 microns are used as anodes and plaques with porosity in the range 70-80% with pore dia 10-15 microns are used as cathodes [3]. The anode is stabilized by using mixed powders of Ni-Cr, Ni-Al or refractory oxides and sintered at 1173-1373 K, under a reducing atmosphere to provide creep resistant anode structure [4-7]. The cathodes are usually made by the same method as the anode and then in-situ oxidized and lithiated to $Li_xNi_{1-x}O$ during cell operation [8,9].

There are many methods reported in literature for the preparation of porous sintered nickel structures with adequate porosity and pore size distribution. The electrode performance of MCFC depends on the electrolyte occupation inside the pores. Trials have been made to control the electrolyte occupation of anode and cathode pores within appropriate ranges by optimizing the anode and cathode pore structure [10,11]. The oldest method is the gravity sintering method [12,13]. Improvements have been made by incorporating a bubble barrier layer to control the wetting properties of the anode [14]. Organic binders are used during the cold rolling stage, which is removed during the sintering process [15,16]. Composite coating method was employed to deposit Raney alloys into the nickel matrix [17]. Efficient porous cathodes were synthesized by incorporating a nickel polymer composite into the structure, which was subsequently oxidized in air [18,19].

From the point of view of larger scale fabrication of MCFCs, these processes for preparing the electrodes may not be efficient. To prepare larger area electrodes, slurry/slip casting and tape casting methods [4,20] were adopted as an improvement to the aqueous slurry process [10]. Aqueous tape casting method employs polyvinyl alcohol or methylcellulose as binders. To obtain a fast curing method a non-aqueous process has also been reported [21]. To provide better contact with the electrolyte substrates, preparation of combined tapes by a non-aqueous process [22] and in-cell sintering procedures were adopted [23].

Tape casting method has been described as a versatile method of making smooth, flat and thin substrates with larger geometrical area and found to be a suitable method for preparing fuel cell component [24]. We have investigated the parameters influencing the tape casting of nickel powder by an aqueous slurry process. The binder burnt-out conditions were also evaluated by TGA study. The results are presented.

TABLE I: Materials and composition of three different types of tape casting slips employed for preparing the nickel tapes

Material	Function	Type 1 (wt%)		Type 2 (wt%)		Type 3 (wt%)	
		min	max	min	max	min	max
A	Substrate	46	55	55	60	40	45
B	Binder	4	5	4	5	5	6
C	Plasticizer	8	10	12	18	10	14
D	Solvent	28	40	23	26	35	40
E	Dispersant	0	2	0	2	0	2

A = Nickel powder; B = Polyvinyl alcohol in water (Dry wt content only); C = Glycerol; D = Water and E = Other liquids

EXPERIMENTAL

The nickel powder type INCO 255 was used. The Ni powder was treated in hydrogen atmosphere as described in [25]. The method of preparation of the slurry for the tape casting process involves preparation of slurry of nickel powder in water with suitable binder and plasticizer. Commercial grade reagents available were employed for the process. Three different types of slurries were employed for the studies. They are termed as low - medium (TYPE 1), low - high (TYPE 2) and medium - high (TYPE 3) respectively depending upon the binder and plasticizer contents. The composition was varied in between the maximum and minimum limits as described in Table I to prepare different samples under each category. The extra water addition has been restricted between 0 and 10 wt%.

The milling was done in two stages as described earlier [26]. At the first stage, the dispersant, the binder (PVA liquid 15 wt.%) and defoamer were added to the water followed by nickel powder. The ingredients were mixed thoroughly and the slurry was then ball milled for 3 hr in order to break the weak agglomerates. Then the plasticizer was added to the above suspension and the resulting slurry was ball milled for additional 3 hr. The slurry was slightly warmed, cooled and deaired and then cast using a doctor blade assembly over a glass plate coated with silicone oil or liquid paraffin. The drying was performed slowly at room temperature for about 24 to 36 hr. The cast nickel tape is then stripped off gently from the glass plate and stored.

A PL thermal systems model STA 1500, differential thermal analyser was employed. A heating rate of 10 K/min was employed in air. The results were used to determine the thermal heat treatment schedule to be followed for the

sintering procedure. Sintering was done in hydrogen atmosphere at temperature 1173 K.

The green nickel tapes were characterized for the thickness, shrinkage factor, and density values. The sintered samples were also characterized for sintered density, shrinkage after sintering. The porosity and pore size distribution measurements were carried out using Micromeritics Model 9320 Pore Sizer.

RESULTS AND DISCUSSION

Tape casting with aqueous slurries has several advantages over nonaqueous method in that the former involves handling of nontoxic materials and vapours [27]. The first part of the work was to obtain a crack free green tape. This depends upon the good choice of the constituents of the slurry and on their quantitative optimisation.

The flow chart for the preparation of the tape casting slurry was reported earlier [26]. Typical compositions wherein the total binder content is below 5 wt% are termed as low binder compositions (types 1 and 2) and that with above 5 wt% is termed as medium binder content (type 3) compositions corresponding to binder to nickel ratios below 10% and above 10% respectively. Similarly the compositions wherein the plasticizer content is high (> 10 wt%) with plasticizer to nickel ratios > 25% are grouped under types 2 and 3. The other characteristic ratios were calculated for all the compositions under different types are indicated in Table II. The binder to total liquid ratio increased from type 1 to

TABLE II: Typical characteristics of composition of nickel tape casting slips

Characteristics of slips	Type 1	Type 2	Type 3
Binder/Nickel (wt)	0.09	0.08	0.15
Plasticizer/Nickel (wt)	0.17	0.20-0.24	0.30-0.33
Binder/Plasticizer (wt)	0.54	0.23-0.38	0.45-0.50
Plasticizer/Binder (vol)	0.28	0.40-0.64	0.30-0.34
Binder/(Binder+Plasticizer)(wt)	0.35	0.19-0.27	0.32
Further addition of water	yes no	yes no	yes no
Nickel (total liquid) (wt/vol)	0.86-1.25	1.20-1.40	0.70-0.75
Binder/total liquid (vol/vol)	0.53-0.75	0.60-0.70	0.70-0.75
Plasticizer/total liquid (wt/vol)	0.15-0.20	0.30-0.35	0.20-0.25
Characteristics of tapes			
Shrinkage after casting (%)	40 60	65 70	40 70
Shrinkage after sintering (%)	15 10	10 5	10 5
Green rape density (g/cc)	1.86 3.62	2.26 2.86	1.92 3.05
Sinter density (g/cc)	2.37 3.86	--- 3.97	2.80 3.32
Porosity (%)	65 55	50 45	70 50

type 3. The binder to plasticizer and binder to total binder (binder + plasticizer) ratios were the lowest for type 2. Consequently the nickel to total liquid ratio and plasticizer to total liquid ratios were the highest. Type 3 is considered as a higher liquid content slurry and consequently the nickel to total liquid ratio was the lowest.

Qualitative physical observations were made during the process of milling the slurry like slip nature, viscosity, during the casting process like slip transferability, tape workability and that of the cast ware like surface homogeneity, tape appearance for bumps, blisters, cracks, pin holes etc. No correlation could be made with their composition for these parameters. However the following observations were made. For tapes prepared from slurries with binder content less than 4 wt% (dry wt basis), cracks were noticed during drying and a significant fissuring has occurred during handling them. Similarly when the nickel content was low and the plasticizer content was above 10 wt% oilcloth like appearance was noticed.

The shrinkage factor after casting, during the sintering, the density values of the green and sintered samples and the porosity values are also tabulated in Table II. These values were entirely different for the three different types. Type III slurry resulted in thinner tapes with higher shrinkage factor. Consequently the green tape density values were also lower. The porosity values were the highest reaching 70%. The green tape density and sinter density values decreased from types 1 to 3 as the total binder content increased from types 1 to 3. Because of the higher nickel content in type 2 the porosity values were less than 50%. The tapes with higher

shrinkage factor have higher packed density and lower porosity values.

Variations in the liquid content of the slurry were also done by the addition of water or low molecular weight alcohol to the tape casting slips. While it maintains the binder/solid, plasticizer/ solid and binder/(binder + plasticizer) ratio values to be the same, the solid/liquid, plasticizer/liquid and binder to liquid ratios were lowered with increasing amount of additions. This has resulted in decrease in the thickness of the tapes with uniform surface characteristics. The green density and sinter density values increase resulting in higher packing factor and lower porosity values. As the (binder + plasticizer)/liquid ratio decreases the porosity values also decrease. Similarly the shrinkage factor of the green tapes is high with high liquid content slurries. An important observation noticed is the variation in the green density values as the binder to total binder ratio is changed as shown in Fig. 1. The density values decreased with increase in the binder/(binder + plasticizer) ratio. Plasticizers are added to impart sufficient flexibility to the green tape for easy handling and storage. As the plasticizer amount is increased, it has the same effect on density and porosity values as in the case of the addition of water.

A typical TGA/DTA pattern of the green nickel tape is shown in Fig. 2. Initially there a steady loss in weight by 3 -5% upto 393 K is observed due to removal of water from the green tapes. On further heating, a steep reduction in weight (10%) is noticed upto 473 K due to the removal of the binder. A secondary weight loss ranging from 5 to 7% is noticed upto 553 K due to the removal of the plasticizer. The removal of all the volatile and decomposable organic matter is completed below 673 K, beyond which the oxidation of nickel surface takes place. The total weight loss
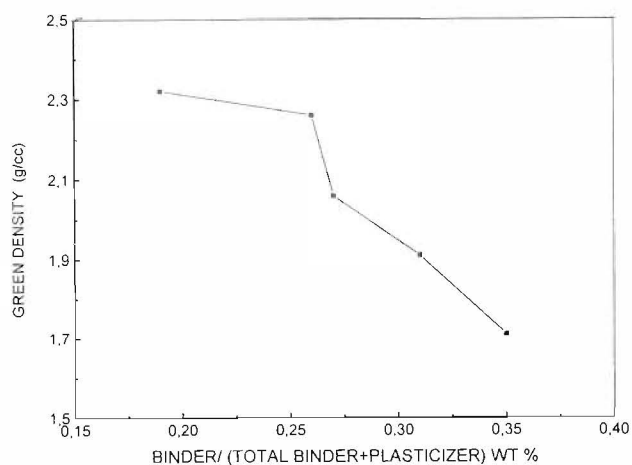

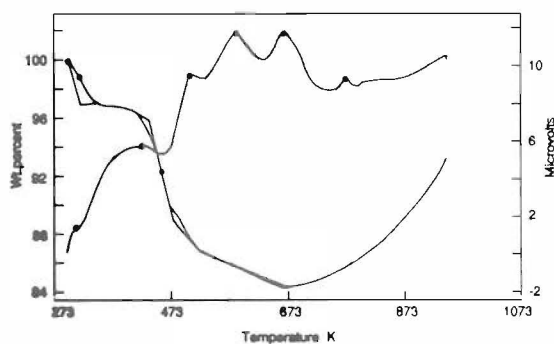Fig. 1: Green density - total binder relationship for the green nickel tapes

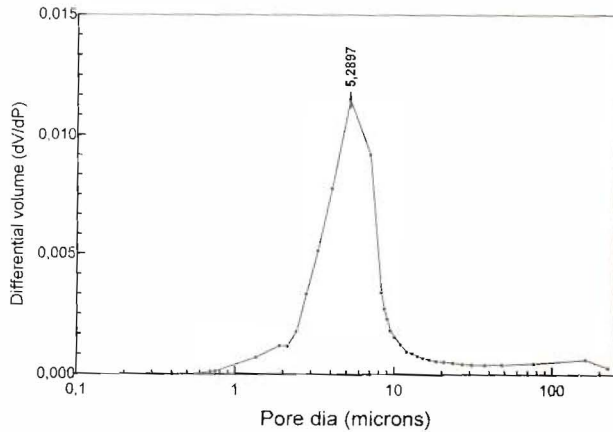Fig. 2: TGA/DTA curve of the aqueous Ni tape

Fig. 3: Pore size distribution curve for the nickel electrode

varies from 20% to 24% depending upon the binder and plasticizer contents in the green tapes. This pattern is quite useful in deciding the heating pattern to be employed for the sintering of the electrodes.

A typical sintering programme consists of the following stages.

  i) Start from room temperature to 403 K at 1 K/min in nitrogen

  ii) Hold the temperature at 403 K for one hour.

  iii) Raise the temperature to 503 K at 1 K/min in nitrogen

  iv) Hold the temperature at 503 K for one hour

  v) Raise the temperature to 673 K at 1 K/min in hydrogen

  vi) Hold the temperature at 673 K for one hour in hydrogen

  vii) Raise the temperature to 1073 K at 1 K/min in hydrogen

  viii) Hold the temperature at 1073 K for one hour in hydrogen

  ix) Cool to room temperature at 1 K/min in hydrogen

The above has resulted in good quality sintered electrodes.

The total penetration volume (pore volume), the average pore dia, the total pore area and porosity values for the sintered electrodes are indicated in Table II. The electrodes with higher porosity have higher penetration volume and higher internal pore area (> 5 m^2/g). The bulk density values were

TABLE III: Porosity and pore size distribution data of some tape cast electrodes

Total pore volume CC/G	Total pore area SQ.M/G	Average pore dia microns	Bulk density G/CC	Apparent density G/CC	Porosity %
0.4015	6.216	5.2426	1.8599	8.3099	77.59
0.3954	6.510	5.4190	1.9151	7.8907	75.73
0.3868	6.233	8.5256	1.9178	7.4296	74.19
0.3357	5.896	7.2882	2.0934	8.0671	74.05
0.3338	5.127	7.3321	2.3992	9.2181	73.97
0.3283	5.575	4.5682	2.1694	7.8653	72.42
0.3270	5.234	9.5536	2.2153	8.0358	72.43
0.3075	5.832	6.2534	2.2241	7.0356	68.39
0.2732	4.369	4.9860	2.5331	7.6006	66.67
0.2681	4.487	3.8472	2.3653	6.9176	65.77
0.2253	4.151	7.3742	2.8143	7.6908	63.41
0.1762	4.538	5.2837	3.5759	8.8127	59.43
0.1668	3.833	6.1930	3.3010	7.9249	58.35
0.1613	0.189	4.5370	3.4301	7.6768	55.32
0.1279	5.762	4.0892	4.3383	9.7492	55.50
0.1252	7.770	4.0763	4.5533	9.5659	54.49
0.1289	2.590	5.2245	4.1114	8.7609	53.04
0.1292	0.125	6.8889	3.4852	7.3017	52.13
0.1226	0.123	4.9940	4.1133	8.2949	50.41
0.1083	0.222	3.4658	3.7849	6.4436	41.10

also lower. The electrodes with lower porosity values have lower penetration volume (0.02-0.1 cc/g). The density values were higher greater than 4.0 m^2/g. The skeletal density values were also higher and the metal powder is closely packed in these electrodes. The pore size distribution pattern for a sintered electrode from group 3 is indicated in Fig. 3. This figure indicates that an electrode with a total porosity of 75%, the average pore size distribution is around 5.5 microns.

CONCLUSION

Good quality nickel electrodes were produced by aqueous tape casting method using PVA as binder and glycerol as the plasticizer. The shrinkage factor of the green tape depends on the binder and plasticizer content of the tape casting slurry. High liquidous slurries produced thin tapes with higher packing density and lower porosity. The composition of the binder and plasticizer amount can be controlled to arrive at optimum dense tapes which can give the desired porosity to the electrodes after sintering.

REFERENCES

1. A J Appleby and F R Foulkes, *Fuel Cells - Hand Book,* Von Nostrand Reinhold, New York (1989)

2. K Joon, *Proc 5th Grove Fuel Cells Symp Conf,* London -1997, *published in J Power Sources,* **71** (1998) 12

3. S S Penner, *Assessment of Research Needs for Advanced Fuel Cells,* U S Dept of Energy, Washington DC (1985) DOE Report No AC-01-84-ER30060 T1

4. Energy Research Corporation, *Final Report,* DOE -ET-11304- 19, Feb-Dec (1980)

5. C D Iacovangelo, *J Electrochem Soc,* **133** (1986) 2410

6. L Paetsch, J Dayon, R Chamberlin and C Yuh, *Electrochemical Soc, Extended Abstracts,* **87-2** (1987) 277

7. Energy Research Corporation, Report No DOE -ET-11304-29, Sep (1983)

8. N Q Minh, *J Power Sources,* **24** (1988) 1

9. E Antoloini, *J Power Sources,* **40** (1992) 265

10. S Mitsuishima, H Okada, M Takeuchi and S Nishimura, *Denki Kagaku,* **60** (1992) 906

11. Y Iwase, H Okada, S Kuroe, S Mitsuishima and M Takeuchi, *Denki Kagaku,* **62** (1994) 152

12. United Technologies Corporation, Report No. DOE-AC-01-89 ET15440, July-Sep (1980)

13. General Electric Co, Report No. SRD-80-055

14. C D Iacovangelo and B R Karas, *J Electrochem Soc,* **133** (1986) 1595

15. V P Bychin, M A Zvesdkin and O M Samatov, *Russ J Electrochem,* **29** (1993) 1173

16. V P Bychin, M A Zvesdkin and O M Samatov, *Russ J Electrochem,* **29** (1993) 1343

17. T Kudo, T Nishina and I Uchida, *Denki Kagaku,* **58** (1990) 354

18. H Numata, H Yamazaki and I Ohno, *Denki Kagaku,* **61** (1993) 747

19. H Numata, N Enami and I Ohno, *Denki Kagaku,* **64** (1996) 378

20. A Pigeaurd, H C Maru, L Paetsch, J Dayon and R Bernad, *in Proc Symp on Porous Electrodes,* Theory and Practice, PV-84-8 (Eds) H C Maru, T Katan and M J Klein, The Electrochemical Soc Inc Pennington, New Jersey (1984) 234

21. E Antolini, F Ferretti and S Gamme, *J Mat Sci,* **31** (1996) 2187

22. J Nikura, K Hatoh, N Taniguchi, T Gamo and T Iwaki, *J Appl. Electrochem,* **20** (1990) 606

23. J Nikura, K Hatoh and T Iwaki, *J Chem Soc Japan,* (1989) 25

24. A S Nesaraj, S J Pores, G Prabhu, K L Anitha, C Solaiyan, S Dheenadayalan, R Chandrasekaran and R Pattabiraman, *Bull Electrochem,* **14** (1998) 354

25. S Dheenadayalan, C Solaiyan, P Gopalakrishnan, R Chandrasekaran and R Pattabiraman, *PMAI News Letter,* **14** (1988) 17

26. G Prabhu, C Solaiyan, I Arulraj, S Muzhumathi, S Dheenadayalan, R Chandrasekaran and R Pattabiraman, *Bull Electrochem,* **15** (1999) 18

27. D Hotza and P Grazil, *Mater Sci and Engg,* **A 202** (1998) 200