



The Effect of Process Parameters on the Apparent Defects of Tape-Cast SOFC Half-Cell

H. Mohebbi ^{a*}, O. Sharifi ^a, M. Golmohammad ^a, A. Molla Ahmad ^a

^a Renewable Energy Department, Niroo Research Institute (NRI), Tehran, Iran

PAPER INFO

Paper history:

Received 27 July 2019
Accepted in revised form 10 December 2019

Keywords:

Tape Casting
SOFC
Anode
Electrolyte
Defect

ABSTRACT

Using flawless components are important for a proper material selection and best working conditions to achieve the best performance of solid oxide fuel cells (SOFCs). Tape casting is the most used process for the fabrication of SOFC parts, especially anode and electrolyte due to its advantages regarding the other processes. In this study, the effect of slurry composition and milling time were successfully investigated on anode and electrolyte tapes defects. The results showed that the addition of terpineol to electrolyte slurry as a dispersant would reduce the size of agglomerates to 5 μ m. Furthermore, 6h of ball milling showed the optimum result for the anode slurry due to the disappearing of island defects, which agrees well with optical microscopy images of samples with minimum apparent defects on the surface. Afterward, the optimum tapes of anode and electrolyte were laminated and sintered at 1400°C for 4h. Half-cells had minimum apparent deformations and surface defects after sintering. Scanning electron microscopy images exhibited a uniform distribution of porosities without any separation in anode layers, as well as the full dense electrolyte.

1. INTRODUCTION

Solid oxide fuel cells (SOFCs) are attracting more attention due to their advantages such as zero emissions, fuel flexibility, high-energy efficiency, and co-generation [1-3]. SOFCs operate based on an electrochemical reaction between oxygen and hydrogen. Generally, a SOFC consists of three main parts, which are anode, electrolyte, and cathode. Hydrogen is oxidized on the anode side and consequently, provides electrons. Electrons move to the cathode side and cause the reduction of oxygen on the electrolyte/cathode interface. Oxygen ions pass through a solid electrolyte commonly 8YSZ and react with oxidized hydrogen in the anode to produce water [4-6].

In recent years, many types of research were carried out to improve the performance SOFCs by optimization of anode and electrolyte layers. Materials selection, compositions, and fabrication process are the most important parameters for researchers [7-9]. Typical materials for the electrolyte are fluorites (YSZ, GDC, and SDC), perovskites (LSGM), or apatites (LSO and LGO). As for anodes, the most frequently used materials are cermet, where the metallic part is typically nickel and

the ceramic component is generally the same material as the electrolyte. Finally, LSM, LSCF, LSC ($\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$), or LSF ($\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$) are the most frequently applied cathode materials [10-13]. The conventional manufacturing process for SOFCs requires more than three steps of heat-treatment at high temperatures to burn-out supports, sinter the electrolyte, and fire the cathode. These heat-treatments during SOFC fabrication account for most of the manufacturing time and consume a lot of energy. A co-sintering process of multi-layer structures yields significant benefits in time, effort, and energy savings, for SOFC manufacturing. The successful application of this technique would increase production throughput and decrease energy usage [14-18]. The microstructures of the electrodes and electrolyte, as well as the density of the electrolyte, need to be considered when performing a high temperature single-step co-firing. Electrolyte sintering is one of the significant factors that affect the co-firing temperature, which can be decreased by the deposition method or metal oxide addition to the electrolyte as a sintering aid [19].

Tape casting is the basic fabrication process that provides multilayered ceramic packages. Tape casting is very

* Corresponding Author Email: hmohebbi@nri.ac.ir (H. Mohebbi)

simple compared with other conventional ceramic preparation techniques and requires only basic equipment [20-23], which also makes it possible to produce a SOFC single cell (anode-electrolyte bilayer) by single-step co-firing. In tape casting, the behavior of the slurry, as well as the material flow during casting, are very important. These parameters determine the final properties and hence, the quality of the cast product. As a result, an increasing number of works in literature were conducted during the last decades within fluid flow analysis of tape casting, the effect of viscosity, particle size distribution, and solid loading [24,25]. The effect of milling time after binder addition, tapes thickness, and slurry ingredient addition sequencing were less considered in the conducted studies. In this research, the effect of some process parameters such as milling time after binder addition and dispersant usage was studied for anode and electrolyte layers.

2. MATERIALS AND METHODS

Anode slurry was prepared by mixing ceramic powders (NiO-8YSZ), solvent (toluene and ethanol), pore-former (starch), dispersant (terpineol), and plasticizers (Benzyl butyl phthalate (BBP)) in a ball-mill with 5mm YSZ balls as grinding media. After 16 hours of ball milling, 3%wt binder (Poly Vinyl Butyral (PVB)) was added, and milling continued for 2, 4, 6, and 8 hours. The composition of anode slurry is shown in Table 1. Anode green tape with a thickness as much as 80 μ m was tape-casting by a lab cast machine, and dried at room temperature for 24 hours.

Electrolyte slurry was prepared in the same way as anode slurry. The recipe is shown in Table 2. A slurry was prepared without terpineol as the dispersant for comparison. Electrolyte green tape was tape casting with a thickness as much as 20 μ m as the same procedure with the anode. Table 3 summarizes the prepared anode and electrolyte tapes.

TABLE 1. Composition of anode slurry

| Material | Role in slurry | Weight percent | Producer |
|-----------|----------------|----------------|-------------------|
| NiO-8YSZ | Anode powder | 42 | Fuelcellmaterials |
| Ethanol | solvent | 24 | Merck |
| Toluene | solvent | 24 | Merck |
| Starch | Pore-former | 4 | Merck |
| Terpineol | dispersant | 0.4 | Merck |
| BBP | plasticizer | 2.8 | Sigma Aldrich |
| PVB | binder | 2.8 | Sigma Aldrich |

TABLE 2. Composition of electrolyte slurry

| Material | Role in slurry | Weight percent | Producer |
|-------------|--------------------|----------------|---------------|
| 8YSZ | Electrolyte powder | 50 | Tosoh |
| MEK | solvent | 21.3 | Merck |
| isopropanol | solvent | 21.3 | Merck |
| Terpineol | dispersant | 0.4 | Merck |
| BBP | plasticizer | 3.5 | Sigma Aldrich |
| PVB | binder | 3.5 | Sigma Aldrich |

TABLE 3. Prepared anode and electrolyte tapes

| Sample | Tape | Ball milling after binder addition | Dispersant |
|-----------|-------------|------------------------------------|------------|
| an-2h-te | anode | 2 h | terpineol |
| an-4h-te | anode | 4 h | terpineol |
| an-6h-te | anode | 6 h | terpineol |
| an-8h-te | anode | 8 h | terpineol |
| el-2h-te | electrolyte | 2h | terpineol |
| el-4h-te | electrolyte | 4h | terpineol |
| el-6h-te | electrolyte | 6h | terpineol |
| el-8h-te | electrolyte | 8h | terpineol |
| el-10h-te | electrolyte | 10h | terpineol |
| el-2h | electrolyte | 2h | - |
| el-4h | electrolyte | 4h | - |
| el-6h | electrolyte | 6h | - |
| el-8h | electrolyte | 8h | - |
| el-10h | electrolyte | 10h | - |

The defect-free green tapes were dried at room temperature for 12 hours. One electrolyte tape was laminated on five anode layer with a laminator (Desktop Laminator 110-AX) machine and was sintered at 1400 $^{\circ}$ C for 4 hours according to the procedure shown in Figure 1 to produce a SOFC half cell. The optical microscopy (SAIran - ZSM1001) and grindometer were used to evaluate the quality of prepared tapes and the presence of agglomerates in tapes. The microstructure of the half cell was studied using a scanning electron microscopy (VEGA-TESCAN II).

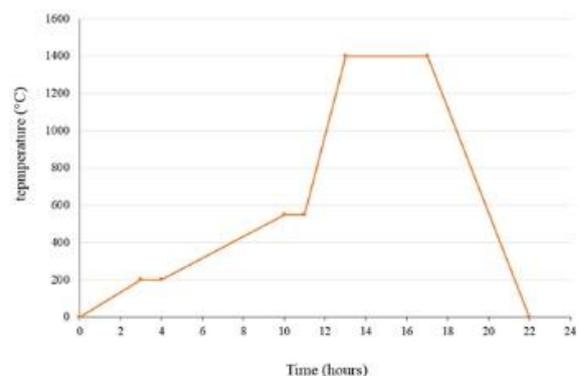


Figure 1. Heating profile for half cell sintering

3. RESULTS AND DISCUSSION

The surface images of anode tapes, which casted at different times after binder addition are shown in Fig. 2. The island features, as well as the surface non-uniformity, can be seen in the samples with shorter milling times. These features are visible even with unaided eyes (Fig. 3). A short mixing time does not allow the complete solubility of the binders or perfect polymer cross-linking, which leads to heterogeneous drying that has been seen by other researchers [15,16]. The amount and the size of these features decreased and completely disappeared after 6 hours milling by increasing milling time after binder

The surface of the samples became a bit shiny by increasing milling time. Whatever the milling times led to the excessive dissolution of the binder and migration to the surface by the solvent during the drying process, consequently, the amount of precipitated binder on the surface increases. The sticky characteristic of the surface confirms the binder migration. The quality of green tape directly affects the sintered anode. As shown in Fig. 4, the quality of an-6h-te sample (Fig. 4A) was much better than an-2h-te sample (Fig. 4B). According to the above results, the optimum time for milling the anode slurry after binder addition is 6 hours.

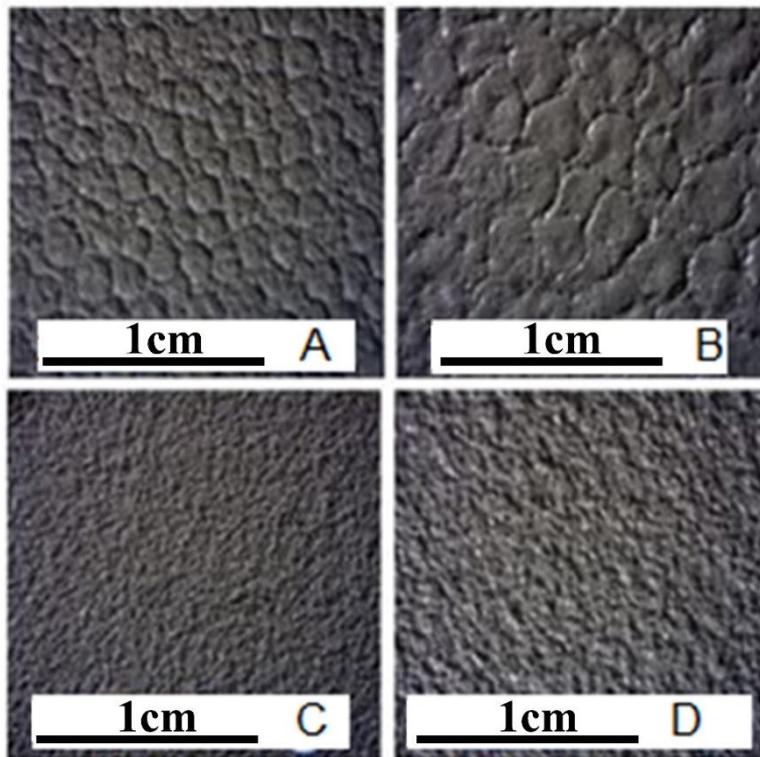


Figure 2. Optical microscopy image of Anode surfaces A) an-2h-te, B) an-4h-te, C) an-6h-te and D) an-8h-te

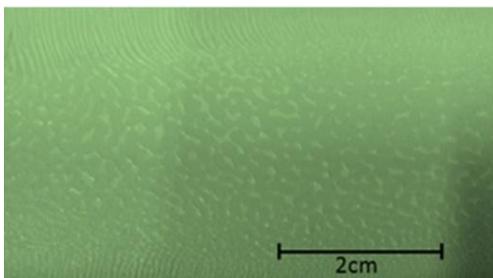


Figure 3. Digital photo of an-2h-te surface

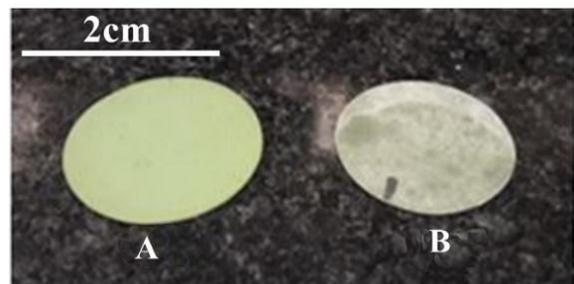


Figure 4. Sintered anode A) an-6h-te and B) an-2h-te

The optical microscope image of the surface of the el-2h sample is shown in Fig. 5A. The presence of large amounts of agglomerates is evident in the tape. The number of agglomerates and their size was reduced without terpineol by increasing the milling time, but they were not completely disappeared even though after 24 hours of ball milling.

The results showed that terpineol has a considerable effect on agglomerates as dispersant (Table 4). In the same milling time, terpineol reduces the size of agglomerates and disappears agglomerate at shorter ball-milling times. Agglomerates size reduced to less than $5\mu\text{m}$ with terpineol after 6h of ball milling, which was not visible on green electrolyte tape (Fig. 5B). However, other types of research reported a longer time of ball-milling as long as 24h for complete dispersion, which might be due to the nature of applied dispersant [15,25]. Therefore, the optimum time for electrolyte slurry ball-milling after binder addition was 6h in the presence of terpineol. Therefore, a perfect green electrolyte tape is impossible without terpineol.

TABLE 4. Agglomerate size in electrolyte tape

| Ball mill time after addition binder (h) | Agglomerations size | |
|--|---------------------|-------------------|
| | With terpineol | Without terpineol |
| 2 | <10 μ | <50 μ |
| 4 | <10 μ | <50 μ |
| 6 | <5 μ | <50 μ |
| 8 | <5 μ | <30 μ |
| 10 | <5 μ | <30 μ |
| 24 | <5 μ | <15 μ |

The microstructure of the half-cell prepared from the optimum anode tape and the optimum electrolyte tape is shown in Fig. 6. The thickness of the anode layer is about $413\mu\text{m}$ and the porosity has spread uniformly throughout the anode. Furthermore, there is no evidence of a poor connection between anodic layers, as well as electrolyte and anode layers. The electrolyte is almost fully dense (Fig. 6B), and no defect is observed. The resulting microstructure is a typically suitable microstructure for a SOFC half cell.

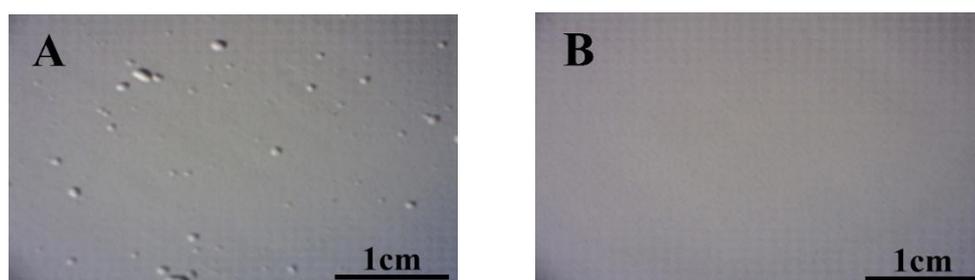


Figure 5. Surface optical microscopy of A) el-2h and B) el-6h-te sample (300X)

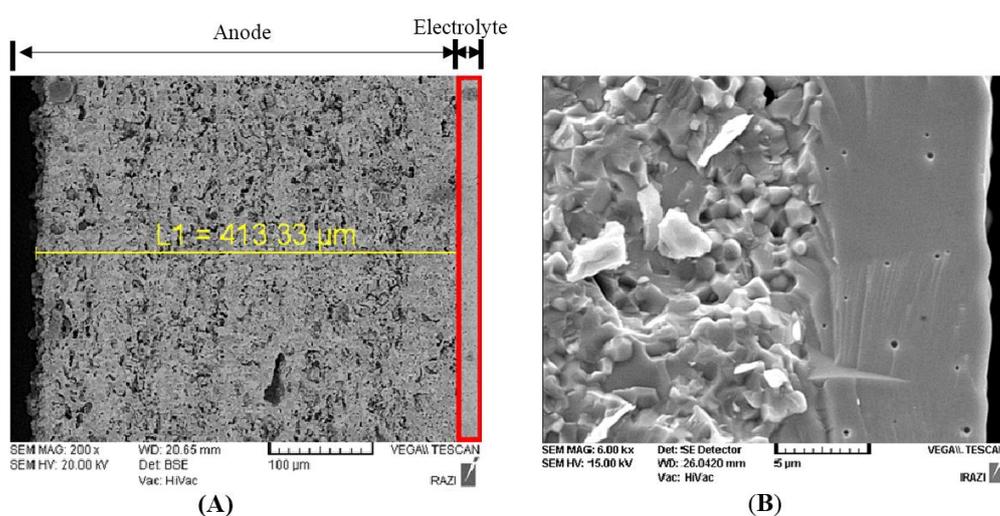


Figure 6. SEM image of the cross-section of sintered half cell; A) 200X, B) 6000X

4. CONCLUSION

In tape casting, the ball-milling time is an important parameter to reach a perfect tape after binder addition. In short milling time, binder is dissolved incompletely, and migrated to the tape surface during drying in long milling time. Both of them deteriorated the quality of green tapes. The optimum milling time after binder addition was 6 hours for anode slurry.

Terpineol was used successfully as a dispersant in electrolyte slurry. A perfect green electrolyte tape is impossible without terpineol. Milling the electrolyte slurry 6 hours after binder addition disappeared the agglomerates in the presence of terpineol, and an acceptable green electrolyte tape was achieved. The achieved SOFC half-cell showed a perfect quality and microstructure with appropriate milling time, which could be used to produce SOFC button cell.

5. ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of Niroo Research Institute (NRI).

REFERENCES

- Haile, S.M., "Fuel Cell Materials and Components", *Acta Materialia*, Vol. 51, No. 9, (2003), 5981- 6000.
- Singhal, S.C., "Advances in Solid Oxide Fuel Cell Technology", *Solid State Ionics*, Vol. 135, No. 1-4, (2000), 305-313.
- Singhal, S.C., "Solid Oxide Fuel Cells for Stationary, Mobile, and Military Applications", *Solid State Ionics*, Vol. 152, (2002), 405-410.
- Minh, N.Q., "Solid Oxide Fuel Cell Technology - Features and Applications", *Solid State Ionics*, Vol. 174, No. 1-4, (2004), 271-277.
- McIntosh, S., Gorte, R.J., "Direct Hydrocarbon Solid Oxide Fuel Cells", *Chemical Reviews*, Vol. 104, No. 10, (2004), 4845-4865.
- Torabi, M., Golmohammad, M., Abdoli, H., Mohebi, H., Azari K., Mehranjani, A., Bozorgmehri, S., "Experimental Investigation of a Solid Oxide Fuel Cell Stack using Direct Reforming Natural Gas", *Iranian Journal of Hydrogen & Fuel Cell*, Vol. 4, No. 4, (2017), 301-306.
- Kim, S.D., Moon, H., Hyun, S.H., Moon, J., Kim, J., Lee, H.W., "Nano-composite Materials for High-performance and Durability of Solid Oxide Fuel Cells", *Journal of Power Sources*, Vol. 163, No. 1, (2006), 392-397.
- Kim, S.D., Moon, H., Hyun, S.H., Moon, J., Kim, J., Lee, H.W., "Performance and Durability of Ni-Coated YSZ Anodes for Intermediate Temperature Solid Oxide Fuel Cells", *Solid State Ionics*, Vol. 177, No. 9-10, (2006), 931-938.
- Kim, S.D., Moon, H., Hyun, S.H., Moon, J., Kim, J., Lee, H.W., "Ni-YSZ Cermet Anode Fabricated from NiO-YSZ Composite Powder for High-Performance and Durability of Solid Oxide Fuel Cells", *Solid State Ionics*, Vol. 178, No. 21-22, (2007), 1304-1309.
- Biswas, M., Sadanala, K.C., "Electrolyte Materials for Solid Oxide Fuel Cell", *Journal of Powder Metallurgy and Mining*, Vol. 2, No. 117, (2013), 2.
- Torknik, F.S., Choi, G.M., Maghsoudipour, A., Kianpour Rad, M., "Nanostructuring Platinum Nanoparticles on Ni/Ce_{0.8}Gd_{0.2}O_{2-δ} Anode for Low Temperature Solid Oxide Fuel Cell via Single-step Infiltration: A Case Study", *Advanced Ceramic Progress*, Vol. 4, No. 1, (2018), 45-51.
- Shaikh, S.P., Muchtar, A., Somalu, M.R., "A Review on the Selection of Anode Materials for Solid-Oxide Fuel Cells", *Renewable and Sustainable Energy Reviews*, Vol. 51, (2015), 1-8.
- Sun, C., Hui, R., Roller, J., "Cathode Materials for Solid Oxide Fuel Cells: A Review", *Journal Solid State Electrochemistry*, Vol. 14, No. 7, (2010), 1125-1144.
- Moon, H., Kim, S.D., Hyun, S.H., Kim, H.S., "Development of IT-SOFC Unit Cells with Anode-Supported Thin Electrolytes via Tape Casting and Co-Firing", *International Journal of Hydrogen Energy*, Vol. 33, No. 6, (2008), 1758-1768.
- Moon, H., Kim, S.D., Park, E.W., Hyun, S.H., Kim, H.S., "Characteristics of SOFC Single Cells with Anode Active Layer via Tape Casting and Co-Firing", *International Journal Hydrogen Energy*, Vol. 33, (2008), 2826-2833.
- Myung, J.H., Ko, H.J., Park, H.G., Hwan, M., Hyun, S.H., "Fabrication and Characterization of Planar-Type SOFC Unit Cells Using the Tape-Casting/Lamination/Co-Firing Method", *International Journal of Hydrogen Energy*, Vol. 37, No. 1, (2012), 498-504.
- Seccombe, D., "Single-step Co-Firing Technique for SOFC Fabrication", In *Advances in Solid Oxide Fuel Cells: A Collection of Papers Presented at the 29th International Conference on Advanced Ceramics and Composites, Jan 23-28, 2005, Cocoa Beach, FL* (Vol. 290, p. 25), (2019, September), John Wiley & Sons.
- Ye, G., Ju, F., Lin, C., Gopalan, S., Pal, U., Seccombe, D.A., "Low-cost Single-Step Co-Firing Technique for SOFC Manufacturing", *ECS Proceedings Volumes*, Vol. 2005, (2005), 451-459.
- Mehranjani, A.S., Cumming, D.J., Sinclair, D.C., Rothman, R.H., "Low-temperature Co-Sintering for Fabrication of Zirconia/Ceria Bi-Layer Electrolyte via Tape Casting Using a Fe₂O₃ Sintering Aid", *Journal of the European Ceramic Society*, Vol. 37, No. 13, (2017), 3981-3993.
- Costa, R., Hafsaoui, J., de Oliveira, A.P.A., Grosjean, A., Caruel, M., Chesnaud, A., Thorel, A., "Tape casting of Proton Conducting Ceramic Material", *Journal of Applied Electrochemistry*, Vol. 39, No. 4, (2009), 485-495.
- Ferrari, E., Ghisolfi, E., Amelio, C., Baccaro, S., "MCFC Matrix: A Comparison Between the Traditional Tape Casting Process and The Upgraded Plastic Extrusion Technology Set up by FN", *International Journal of Hydrogen Energy*, Vol. 36, No. 13, (2011), 8094-8097.
- Straue, N., Rauscher, M., Dressler, M., Roosen, A., "Tape Casting of ITO Green Tapes for Flexible Electroluminescent Lamps", *Journal of the American Ceramic Society*, Vol. 95, No. 2, (2012), 684-689.
- Ghatee, M., Salihi, H., "Investigation of the Mechanical Properties of Various Yttria Stabilized Zirconia Based Thin Films Prepared by Aqueous Tape Casting", *Advanced Ceramic Progress*, Vol. 3, No. 1, (2017), 26-30.
- Bitterlich, B., Lutz, C., Roosen, A., "Rheological Characterization of Water-Based Slurries for the Tape Casting Process", *Ceramics International*, Vol. 28, No. 6, (2002), 675-683.
- Gu, S.I., Shin, H.S., Yeoa, D.H., Nahmb, S., "Effects of the Particle Size and Organic Content of YSZ on Sheet Properties", *Journal of Ceramic Processing Research*, Vol. 13, No. 5, (2012), 556-560.