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The unification of paste rheologies for the co-extrusion of solid oxide fuel cells

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Abstract

Current methods used to manufacture solid oxide fuel cells (SOFCs) involve multiple steps, applying successive layers to produce laminated components associated with repeated sintering steps. This work aims to cut the number of processing steps involved by co-extruding a complete SOFC tube from pastes in a single step, which is then co-sintered. Several aspects must be overcome in order to co-extrude such a fuel cell. Crucially the co-extrusion process requires that the rheological properties of the materials are well matched. This prevents the formation of flow defects and allows for the continuous operation of the co-extrusion process. This work has investigated the manipulation of the rheological parameters through design of the paste formulation as well as the manufacturing process.

Two pastes, one made from a fine yttria stabilised zirconia (YSZ) and the other from a combination of a fine YSZ, a coarser nickel oxide and activated carbon, have been characterised using the Benbow/Bridgwater model and their parameters have been unified through adjustment of their solids loading. Using packing theory and the assumption that pastes will only flow when the powder void space has been filled with a slight excess of liquid to overcome inter-particulate friction, an intermediate paste has been designed to possess similar rheological properties.

Keywords: Co-extrusion; Solid oxide fuel cell; Paste rheology

1. Introduction

Solid oxide fuel cells (SOFCs) are considered to offer a highly efficient, environmentally friendly solution to the growing problem of providing sustainable power generation for the future. Fuel cells electrochemically convert the chemical potential energy contained in fuels directly into electrical energy. They work in a similar manner to batteries, except that fuel cells are designed to be continuously replenished with the reactants as they are consumed, and their electrodes are catalytic and are therefore not used up. Fuel cells are typically designed to run on hydrogen and oxygen, but can be run on other fuels.

There are a variety of fuel cells available, but of particular interest here are the SOFCs, which are in essence a combination of functional ceramics.

The SOFC uses a non-porous ceramic material as the electrolyte, which is typically zirconia that only permits the transfer of oxygen ions. The anode and the cathode are usually made of porous ceramic and cermet materials, through which electrons, gases and ions can travel. The most common materials used for the anode and cathode material are NiO/YSZ cermets and strontium doped lanthanum manganite respectively. However many other materials, such as gandolinia doped ceria (electrolyte) or lanthanum nickel ferrite (cathode), may be considered where co-processing is being proposed (Fig. 1).

SOFCs come in two main forms: a planar design where the fuel cells are stacked together or as tubular structures. Current planar manufacturing methods involve adding layers onto a prefabricated anode or cathode support. This allows for the manufacture of thin electrolyte layers, helping to improve the power density of the fuel cell. However these processes require many processing and sintering steps, increasing the production costs of the fuel cell. Self-supporting SOFCs use much thicker electrolytes, but co-processing potentially allows manufacture to be carried out in fewer steps, as the electrolyte can be manufactured and sintered with the anode and/or the cathode.

Co-sintering presents its own problems due to thermo-physical incompatibilities between the materials. During

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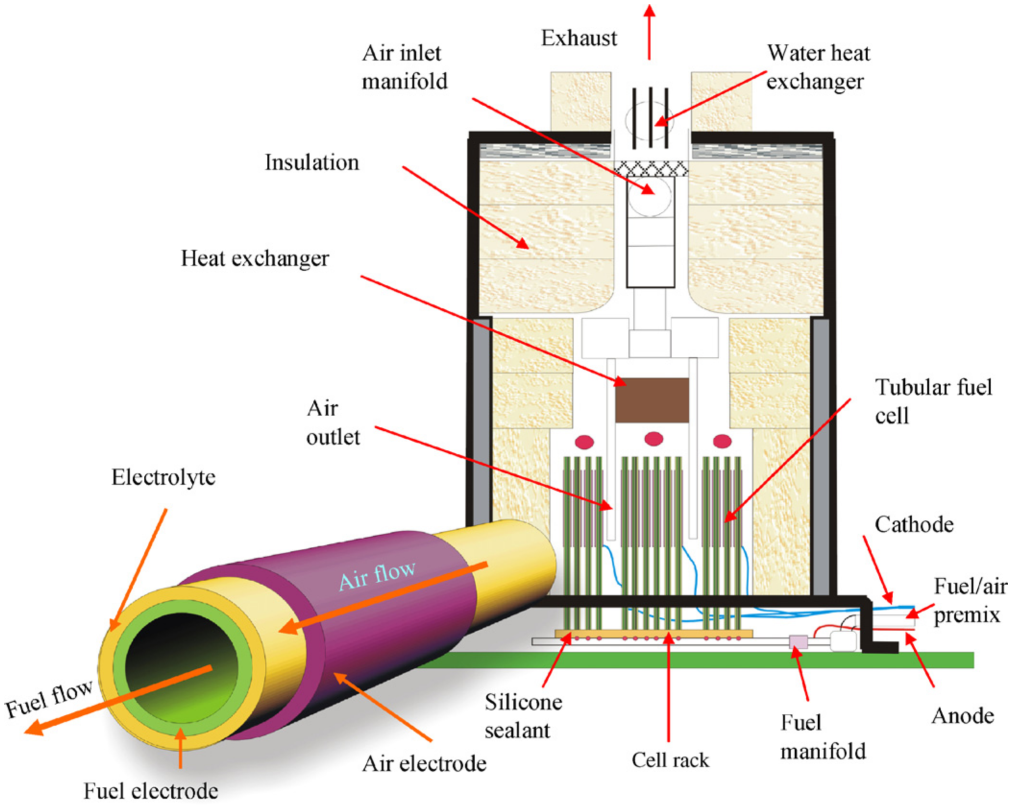

Fig. 1. Schematic of a self-supporting SOFC and its proposed use in a domestic combined heat and power unit.

cooling, residual stresses in the SOFC structure can cause cracking due to differences in thermal expansion and thermal expansion rates. It is therefore important to match materials, so that these stresses are minimized. One method of doing this is to use a functionally graded design, where the two materials are connected by intermediate layers made with graduated compositions changing from one layer to the next. As well as reducing the thermal and residual stresses this structure also increases the number of triple phase sites, where the electrons, gas and ions meet to electrochemically react.

The manufacture of a multilayered self-supported tubular SOFC in a single manufacturing step also poses its own difficulties. The co-extrusion of multiple pastes requires fine tuning and unification of the paste rheologies in order to prevent the formation of flow defects and to allow the use of continuous extrusion. This, therefore, requires the formulation of a number of pastes containing powders with differing particle sizes, size distributions, morphology and surface chemistry, as well as pore size, distribution and shape. Previous works by Liang and Blackburn[1,2] have looked at the co-extrusion of multilayered tubes.

This paper examines the matching of two paste rheologies, which will form the YSZ electrolyte and the NiO/YSZ anode (80/20, w/w). Using packing theory and the measured rheological parameters, the required liquid content of a third paste has been predicted in order to obtain three pastes of similar rheology. A methodology is proposed for the prediction of paste formulations for the formation of a complete anode–electrode structure.

2. Experimental procedure

2.1. Materials

The electrolyte paste was prepared using an yttria stabilized zirconia powder HSY8 (Daiichi Kigenso Kagaku Kogyo Co., Japan), which has an average particle size of 0.5 μm. The anode pastes were made up as mixtures of HSY8, black nickel oxide (−325 mesh, Cerac, USA), and activated carbon (Norit, UK), which acted as a pore forming agent. A proprietary organic binder (FMG, UK) was fixed throughout the experiments.

2.2. Paste preparation

The powders were mixed thoroughly in the dry state prior to wetting. The liquid was added to the powder and the material was then transferred to one of two mixers, a twin roll mill and a z-blade kneader (Werner and Pfleiderer, D).

The material was mixed for a total of 15 minutes on the twin roll mill. The paste was finally removed as a sheet and rolled into rods ready for laying up into the extruder. This method of mixing is limited in terms of sample size and is open to the atmosphere limiting the mixing period due to loss of binder. The twin roll mill can only mix pastes over a narrow range of solid loadings. When the solids loading is too low, the paste is not sheared effectively and cannot be removed from the mill. If the solids loading is too high, the paste becomes unworkable in later processes.

In the z-blade kneader the material was mixed for a total of 4.5 h inside a small sealed unit, kept cool using a supply of water through a jacket. Material was removed from the sides of the container and the blades intermittently to ensure thorough mixing. A much wider range in solids loadings could be made using this mixer, making it possible to produce pastes with a wider range of rheologies.

All pastes were left to equilibrate for half an hour after mixing and before extrusion, therefore eliminating any time dependent variation between pastes.

The initial anode pastes were made up with 30% carbon, 56% NiO and 14% HSY8 by weight. The carbon was added to give porosity to the anode. Each paste was manufactured using the same binder system formulation. The electrolyte and the anode pastes were made to a selection of solids loadings, working to the limits of the mixing and the extrusion process.

2.3. Paste characterization

The paste rheological parameters were evaluated by capillary rheometry using a ram extruder driven by a compression load frame. The 20.3-mm diameter barrel was fitted with interchangeable dies of 6.0 mm diameter, and lengths 8.0, 24.0 and 47.3 mm. The die entry angle was 90°. The pastes were extruded by adjusting cross head speed, giving extrudate velocities ranging from 5.000 to 0.125 mm s^{-1}. The data was then used to characterised the pastes by applying the Benbow/Bridgwater six parameter equation[3–5]

$$P = P_1 + P_2 = 2(\sigma_0 + \alpha V^m)\ln\left(\frac{D_0}{D}\right) + 4\left(\frac{L}{D}\right)(\tau_0 + \beta V^n) \tag{1}$$

where P is the total pressure drop and P_1 and P_2 are the pressure drops due to convergent flow and plug flow respectively. D_0 is the barrel diameter, D is the die diameter, L is the die length and V is the extrudate velocity. The convergent flow yield stress is represented by σ_0 and the plug flow initial wall shear stress is represented by τ_0. β and α are the velocity factors, that represent the velocity dependency of the bulk and the wall shear stress respectively and are related to viscosity in liquid shear flow. V, the extrudate velocity, can therefore be related to the shear rate. m and n are the velocity exponents relating to bulk and wall shear stress respectively. For the most part these are not reported in this text and fixed at a nominal value but are evident from the curvature of the theoretical fits in Fig. 2.

A series of pastes which varied in solids loading were tested both for the electrolyte paste and the end member anode paste. The relationship between the paste rheological parameters and the solids loading could then be analysed. From this information it was possible to predict the required solids loadings for pastes with intermediate compositions, made up from components in the electrolyte and the anode pastes that possess similar rheological parameters. For the purposes of this study a six parameter model was employed to characterise the paste flow behaviour. However only the yield stress and velocity factors were used to match the paste rheologies.

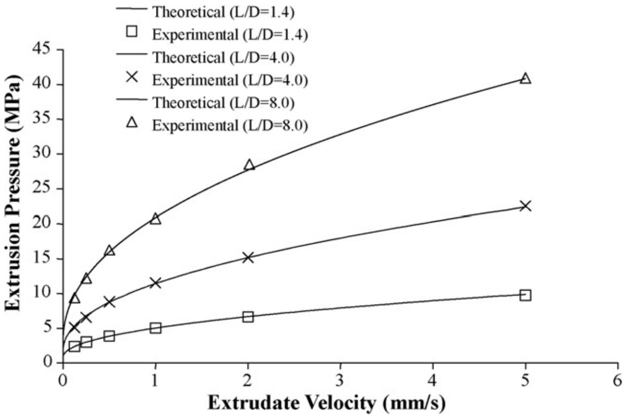

Fig. 2. Benbow/Bridgwater model and experimental extrusion data.

3. Results and discussion

The paste rheological parameters were obtained using the Benbow/Bridgwater fit. The parameters were put back into the equation and the fitted extrusion pressures plotted with the experimental data, as shown in Fig. 2. The relationship offers an accurate representation of the experimental data, and fitted the experimental data with typical R^2 values of 0.99. A plot of extrusion pressure versus L/D can also indicate how well a paste is mixed and for most pastes this plot gave a linear relationship, showing that the paste is not changing along the die land as it is extruded. However for low liquid contents the data tended to deviate from this linear relationship, indicating that the pastes were not being adequately mixed, or that they were more sensitive to localized loss of solvent giving an inhomogeneous paste.

Data for the bulk yield stress (σ_0) is represented in Fig. 3. It has been shown previously by Benbow et al.[3] and Blackburn and Böhm,[6] that there is an approximate linear relationship between the reciprocal parameters and the liquid content. It has also been shown that pastes are unextrudable when containing less liquid than that required to fill the inter-particulate voids. Therefore the intercept of the plotted line on the x axis can, by conversion, give an approximation of the void volume in-between the packed particles at maximum random packing.

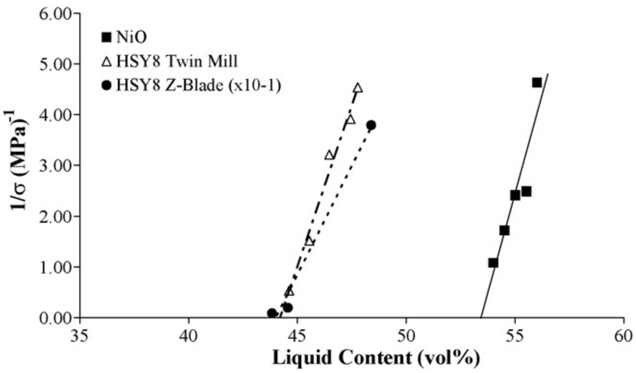

Fig. 3. Relationship between the reciprocal convergent flow yield stress and the paste liquid content.

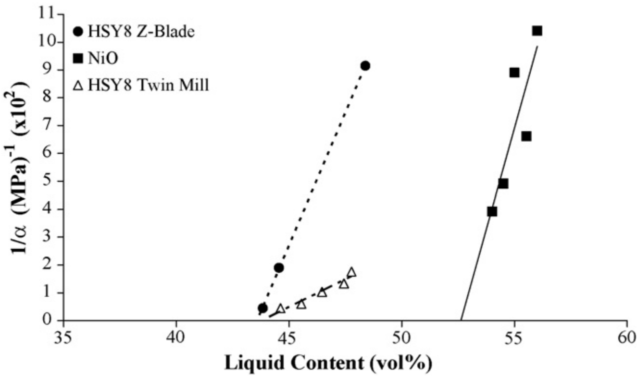

Fig. 4. Relationship between the reciprocal convergent velocity factor and the paste liquid content.

Table 1
Rhelogical parameters and liquid content of the rheologically unified pastes

	Anode paste	z-Blade-mixed electrolyte paste
Liquid (vol%)	17.74	11.70
σ_0	1.01	0.67
α	23.30	23.30
β	5.33	10.56
τ_0	0.11	0.11

The method by which the Benbow/Bridgwater parameters are sequentially calculated causes a decrease in the accuracy of some parameters. As σ_0 and α are the first to be calculated they give the most consistent results, which can be seen in Figs. 3–6. It was possible to fit straight lines to all the plots of $1/\alpha$ and $1/\sigma_0$ using least squares regression, however the parameters $1/\beta$ and $1/\tau_0$ did not always follow a linear relationship with the liquid content of the paste.

In the case of the NiO–C–ZrO_2 pastes the $1/\tau_0$ data implies that for the range of solid loadings analysed, the initial wall shear stress decreases with increasing solids loading. The carbon used in these formulations has a very high surface area and considerable work is required to force the liquid phase to fully wet the system. This occurs most readily in the pastes with lower liquid contents where better mixing is achieved. In the opposite sense, it is possible that the higher pressures required for extrusion at low liquid contents, are insufficient to release the liquid tied up in the carbon after mixing and lubricate the die walls.

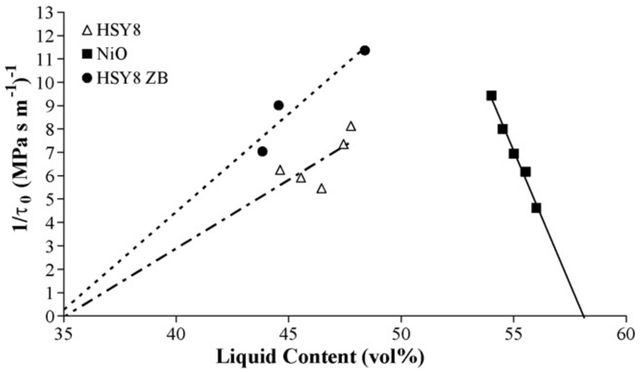

Fig. 5. Relationship between the reciprocal wall shear yield stress and the paste liquid content.

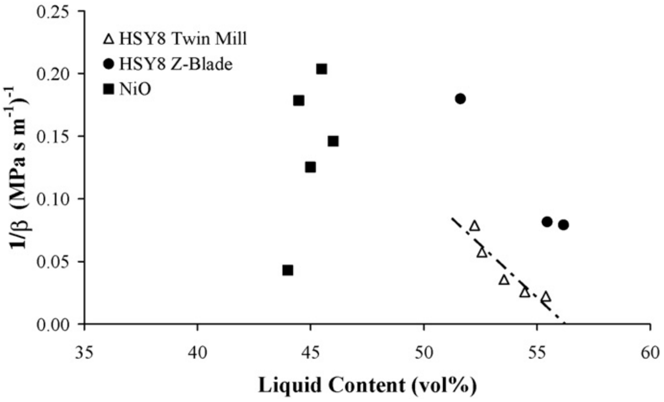

Fig. 6. Relationship between the reciprocal wall shear velocity factor and the paste liquid content.

Data has not been presented here for a z-blade mixed anode paste, as that mixer was unable to produce a paste with these materials; this is probably due to insufficient shear stress being applied to the system.

The electrolyte pastes produced using the two different mixers show different rheological behaviour, with the z-blade mixed paste showing a stronger rheological dependence on the solids loading. However the data generated shows, that the minimum liquid content measured from the Benbow/Bridgwater parameters can be accurately measured when mixed by either method. The implication is, that provided sufficient torque can be generated, the two mixers performance is similar, when the free liquid over and above that required to fill the inter-particulate voids is at a minimum, and the expected extrusion pressures are high.

Table 2
Benbow/Bridgwater parameters and RBV values for the intermediate paste

Solids mass fraction	
ZrO_2	0.54
NiO	0.40
Carbon	0.06
RBV	1.73
$\sigma0$	0.81
α	26.28
β	13.15
τ_0	0.13

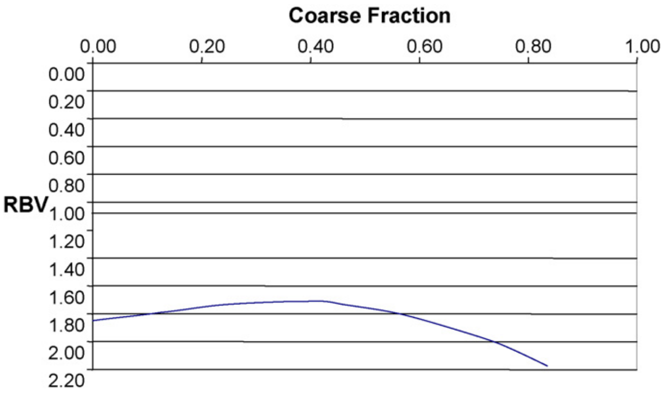

Fig. 7. RBV values for intermediate compositions.

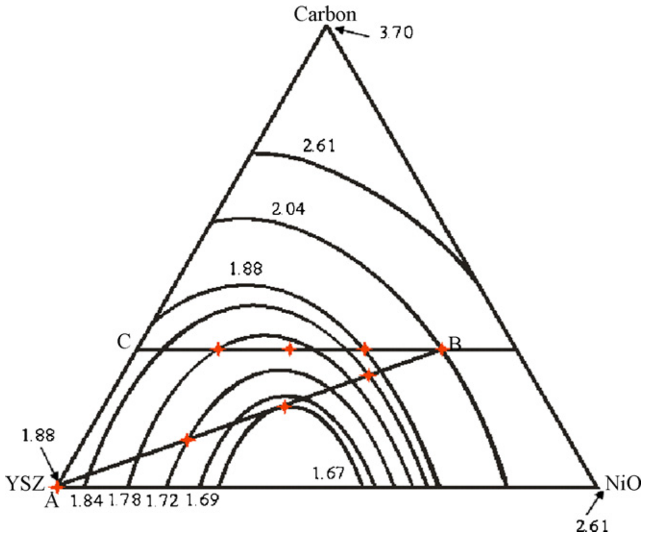

Fig. 8. Composition diagram. Open circles are specimen formulations. Closed circles predicted formulations required for co-extrusion. Curved lines are contours of equal RBV. A is the electrolyte composition. B is the outer anode composition.

Table 1 shows the Benbow/Bridgwater paste parameters and the liquid content of the selected anode and electrolyte paste formulations, which provide the most closely matched rheological parameters. It was found that the closest fit could be achieved, if the electrolyte paste was z-blade mixed, as this provided a broader range in rheological parameters from which to select a match. The range of possible paste parameter values in the twin roll milled pastes was extremely limited particularly for α and β and effective matching was not possible. The parameters were matched in the sequence α, σ_0, τ_0 and β to attain the best compromises in fitting.

From the data presented it is possible to calculate the formulation of any intermediate composition. The intercept of the reciprocal parameters on the x axis can be used to calculate the void fraction of the constituent solids. This leads to the packing fraction (1-void fraction), that can be converted to the relative bulk volume (RBV) for ease of graphical representation. RBV is the reciprocal of the packing fraction. In this case the RBV of the intermediate compositions was calculated using Karlsson and Spring model.[7] Fig. 7 shows the curve obtained from this fit. Reverse calculation from the RBV plot (Fig. 7) allows the volume of liquid required to fill the voids of the composition to be calculated. This, when combined with the average volume of liquid over and above that required to just fill the voids and provide the required paste properties (from Figs. 3–6) allows intermediate paste formulations to be derived.

A paste containing 60% ZrO_2 and 40% NiO by volume (after firing) was formulated following the above procedure and prepared following the standard mixing procedure, then rheologically tested. Its derived parameters are given in Table 2. The parameters are closely matched to the electrolyte and anode pastes and the predicted formulation was therefore appropriate and effective. These pastes are well matched for co-extrusion.

The procedure outlined above assumes that the intermediate compositions have a progressively decreasing addition of the pore forming agent towards the final electrolyte composition which contains no pore forming agent. This may not yield the most ideal structure for optimisation of the fuel cell kinetics in operation, thus a method of calculating the required paste formulations must be considered. The data presented in Fig. 7 is represented by the line AB in Fig. 8. The preferred composition would lie on the line ACB. Within the ZrO_2–NiO–C space a contour plot of RBV derived from $1/\sigma_0 = 0$ can be created using the principles outlined for the bimodal plot shown in Fig. 7. From this data a direct make up of matched pastes should be possible. For any of the proposed compositions shown in Fig. 8, a procedure of reverse calculation could be performed, as described above for the preparation of the intermediate paste formulation, presented in Table 2. Current work is evaluating the success of these predictions.

4. Conclusion

It has been possible to unify the rheology of three pastes. This has been achieved by analysing the relationship between the rheological parameters and the solids loading of the two end member compositions and using that data to predict intermediate packing behaviour. Knowledge of the packing behaviour allowed calculation of the intermediate composition formulations, reducing the number of experiments required to obtain matched rheology. This work has also shown that the method of mixing the paste plays a significant role in the manipulation of the paste rheology.

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