Electronic Supplementary Information

Experimentation and Modelling of Nanostructured Nickel Cermet Anodes for Submicron SOFCs Fuelled Indirectly by Industrial Waste Carbon

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Fig. S1: Schematic representation of the indirect carbon fueled hybrid fuel cell

A 100sccm CO₂ gas enters the bubbler via a CO₂ mass flow controller. The bubbler contains 5g of IWC, placed inside a furnace at which the temperature was kept at 750°C. An inconel 600 grade (APEC Industries, South Korea) was used to filter the by-products of the carbon gasification process. The outlet of the bubbler was fitted to the gas chromatograph (GC) to identify the products of the RBR. The outlet to GC was attached to a H₂ gas supply line with a switch. This hybrid fuel system is connected to the test station setup, where the optimized cell is tested for electrochemical measurement via Solatron.



Fig. S2 (a) Schematic of the old design of the gasifier with little or no CO (b) modification in the bubbler design resulting in higher carbon utilization and hence higher CO.

A 2mm thick inconel plate which has a 20 μ m pore opening. It was tested for good condition and air permeability by the manufacturer. The filter was machined and placed in the outlet of a bubbler. The inconel filter was machined to sit on a stainless steel ring, which was welded to the outlet of the bubbler. A carbon fuel inlet was designed on top of the bubbler, for readily filling up the depleted carbon fuel. CO₂ enters the bubbler and reacts with the carbon inside the bubbler at a high temperature. The resulting CO produced due to the reverse boudouard reaction will then leave the outlet of this bubbler after being filtered from the filter.

In order to maximize the utilization of the carbon fuel, the bubbler design was updated. The new design is shown in Fig. S2(b). The inlet to the bubbler was modified, so that the CO_2 now enters from the base of the bubbler. A second incomel filter is welded just a few centimeters above the base of the bubbler. With this new design the carbon fuel now sits on top of the filter, and almost all of the CO_2 passes through the filter and bubbler after reacting with the carbon. Also with the two filters, the carbon dust does not build up, and allows free passage of the gases without blocking the lines. Hence even unprocessed carbon in raw form can also be used with this new design.



Fig. S3 Long term open circuit voltage (OCV) stability testing for the Industrial waste carbon (IWC) operated fuel cell setup shown in Fig. S1. IWC loading was done at 0,100, and 124hrs of operation



Mapping of the TPBs in the Ni-SDC anode by VEM

Fig.S4 Triple Phase Boundary string mappings for Ni-SDC anode formed by volume expansion method in Image-J.



Fig. S5: BET surface area plots for (a) Pre-operation (b) Post Operation of 100hrs under IWC fuel. Here, Q is the weight of N₂ gas adsorbed at a relative pressure P/P0. P/P0 is the pressure of N₂ gas divided by its saturation vapor pressure. Testing Temperature was 150C and degasifying time was set for 4hrs

Diffusion of species through the anode (Dusty Gas Model)

The two gases were i:CO and j:CO₂, and their diffusion through porous Ni-SDC anode was defined by using Dusty Gas Model (DGM). DGM is written as a relationship of molar flux, molar fraction, and total pressure gradient.

$$\frac{N_i}{D_{i,K}^{eff}} + \sum_{j=1, j\neq 1}^n \frac{X_j N_i - X_i N_j}{D_{ij}^{eff}} = -\frac{P_i}{RT} \nabla X_i - \frac{X_i}{RT} \left(1 + \frac{KP_t}{\mu D_{i,K}^{eff}}\right) \nabla P_t \dots (I)$$

Effective molecular diffusion coefficient can be expressed as a relationship of Volume fraction and tortuosity with Fuller-Schettler Giddings Equation

$$D_{ij}^{eff} = \frac{V_{pore}}{\tau_{pore}} D_{ij} \dots (II)$$

$$D_{ij} = \frac{0.01013 T^{1.75} (\left(\frac{1}{M_i} * 10^3\right) + \left(\frac{1}{M_j} * 10^3\right))^{1/2}}{P((\sum v_i * 10^6)^{1/3} + (\sum v_j * 10^6)^{1/3})^2} \dots (III)$$

Knudsen diffusion is a type of diffusion where the scale length of system is comparable or smaller to the mean free path of the species travelling through that system. In the Ni-SDC porous electrode, it is estimated that the mean free-path of the molecules is larger than the anode pore size, which means the collisions between the molecules and the boundaries of the anode, are more frequent than with other neighboring molecules. Therefore, it is better to use a Knudsen diffusion coefficient to estimate the reactants and products of the reverse boudouard reaction in this case

$$d_p = \frac{4}{\frac{S}{(\frac{S}{V})_{pore}}} \dots (VI)$$

Permeability is defined by combining the Darcy's flow and Poiseuille's flow

$$K = \frac{V_{pore}}{6\tau_{pore} \left(\frac{S}{V}\right)_{pore}^{2}} \dots (VII)$$

We can relate the conservation of gases transported by the Knudsen diffusion, with the charge transfer current by this relation

$$D_{i,K} = \frac{d_p}{3} \sqrt{\frac{8RT}{\pi M_i}} \dots (V)$$

$$\begin{split} \nabla \cdot \left(\frac{k_1}{RT} \nabla P_1\right) + \nabla \cdot \left(\frac{k_1 P_1}{RT} \nabla P_t\right) &= \frac{i_{tpb}}{2F} \dots (VIII) \\ \nabla \cdot \left(\frac{k_2}{RT} \nabla P_2\right) + \nabla \cdot \left(\frac{k_2 P_2}{RT} \nabla P_t\right) &= -\frac{i_{tpb}}{2F} \dots (IX) \\ k_1 &= \frac{D_{12}^{eff} \cdot D_{1,K}^{eff}}{D_{12}^{eff} + D_{12,K}^{eff}} \dots (X) \\ k_2 &= \frac{D_{12}^{eff} \cdot D_{2,K}^{eff}}{D_{12}^{eff} + D_{12,K}^{eff}} \dots (XI) \\ k_{1\prime} &= k_{2\prime} = \frac{K}{\mu} + \frac{D_{12}^{eff} \cdot D_{2,K}^{eff}}{D_{12}^{eff} + D_{12,K}^{eff}} \frac{1}{P_t} \dots (XII) \end{split}$$

Combined effective Knudsen diffusion coefficient is expressed as

$$D_{12,K}^{eff} = X_1 D_{2,K}^{eff} + X_2 D_{1,K}^{eff} \dots (XIII)$$

(δx)

W

W

W

Control Volume

W

W

Non-continuous

point



Since the total pressure is assumed to be constant, hence we can neglect the equations containing P_t terms. Then all the equations take the form of the Poisson-like equation

$$\nabla * (\sigma_{el}^{eff}. \nabla \phi_{el}) = i_{tpb} \qquad , \nabla * (\sigma_{io}^{eff}. \nabla \phi_{io}) = -i_{tpb}$$

 $\nabla * (\Gamma. \nabla \phi) \pm S = 0$

Here S is the source of charge transfer between the electronic and ionic phase. The charge conservation equation is solved for the involved charge transport in the ionic/electronic phase. It involves the solution of the Poisson equations for the ionic/electric field over the entire region.

A 1-D steady state diffusion equation is solved by control volume method (CV) over the entire region to find the solution of this Poisson equation. Fig. S5 shows the control volume schematic representation over a certain point P in consideration.

$$\frac{d}{dx}\left(\Gamma.\frac{d\emptyset}{dx}\right) + S = 0$$

Integrating it inside a control volume from w to e

$$\int_{w}^{e} \left[\frac{d}{dx} \left(\Gamma \cdot \frac{d\phi}{dx} \right) + S \right] dx = 0 \qquad (\Gamma \cdot \frac{d\phi}{dx})_{e} - (\Gamma \cdot \frac{d\phi}{dx})_{w} + \int_{w}^{e} S dx = 0$$

$$\frac{\Gamma(\phi_{E} - \phi_{P})}{(\delta x)_{e}} - \frac{\Gamma(\phi_{P} - \phi_{W})}{(\delta x)_{w}} + S \Delta x = 0 \dots (XIV)$$

Table S1. Boundary conditions for the control volume 1D steady state simulation of the Ni-SDC anode

Parameter	Surface(X=0)	Interface(X=L)
Total Pressure	$P_t(0) = P_t^{bulk}$	$\frac{dP_t}{dx}(L) = 0$
CO partial pressure	$P_{CO}(0) = P_{CO}^{bulk}$	$\frac{dP_{CO}}{dx}(L) = 0$
CO ₂ partial pressure	$P_{CO_2}(0) = P_{CO_2}^{bulk}$	$\frac{dP_{CO_2}}{dx}(L) = 0$
Electric potential in Ni	$\phi_{el}(0) = \eta_t$	$\frac{d\phi_{el}}{dx}(L) = 0$
Electronic & Ionic Potential in SDC	$\frac{d\phi_{el}}{dx}, \frac{d\phi_{io}}{dx} = 0$	$\phi_{el}(L), \phi_{io}(L) = 0$

Here we use a uniform grid system of infinitely small grid points and use the function of circular reference in excel to get the value of the desired point. Since the input value of the point includes the value of that specific point, hence circular reference function in excel gives a viable option. We used a grid system of about 200 points and iterated them over an average of 1000 iterations to give the desired result. For a uniform grid system, $\delta x = \Delta x$, so Eq. XIV re-arranges to

And this is what we basically solve to attain the desired value through circular iterations in excel.