Supplementary Data for: Exploring the combustion synthesis for yttrium ruthenate pyrochlores as OER electrocatalysts

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Contents

S1. Introduction

A schematic illustration representing the course of the combustion reaction can be seen in Figure S1. Furthermore, the fluffy combusted product obtained after the glycine combustion synthesis can be seen in Figure S2.

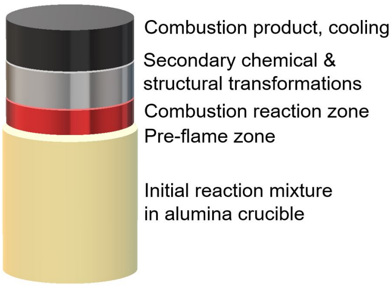

Figure S1: The reaction zones observed during combustion as adapted from Marinšek *et al.*[1]

S2. Choice of precursor

Figure S3 shows pictures of how the Ru precursor used affects the gel formed. When ruthenium chloride is used, a dark brown gel is formed, whereas ruthenium nitrosyl nitrate leads to a light brown gel that has a visibly fluffier appearance (a more voluminous gel).

Figure S2: Appearance of the fluffy product after combustion took place

S3. Choice of fuel

The effect of the fuel used on the appearance of the combusted particles produced can be seen in Figure S4, with alanine pro-

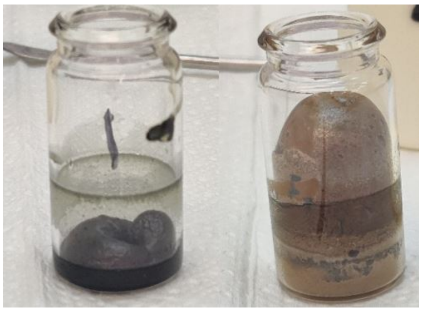

Figure S3: The gel precursor for the combustion synthesis with ruthenium chloride (left) and ruthenium nitrosyl nitrate (right) as precursors.

ducing a visibly less fluffy product than glycine. In this section, we want to mention that polyvinyl alcohol (PVA, MW=9000-10000, Sigma Aldrich) has also been tested as fuel in an attempt to replicate the polymer entrapment flash pyrolysis (PEPF) synthesis as reported by Shih *et al.*.[2] We attempted three different ratios of PVA to precursors. 0.01 g (PEPF1), 0.2 g (PEPF2) and 2.5 g (PEPF3) PVA, respectively, were dissolved in 10 mL DI water and stirred for 8 hours. The PVA solutions were then mixed with 5×10^{-4} mol yttrium nitrate and 5×10^{-4} mol ruthenium nitrosyl nitrate and 0.1 mol nitric acid. The solutions were dried in a water bath at 70 °C and after this in a drying oven at 60 °C overnight. Each of the dried gels were then placed on a hotplate (ca. 200 °C) to facilitate combustion. Only PEPF2 reacted with a violent combustion reaction (a sudden, bright flash), whereas PEPF1 and PEPF3 just turned gradually from brown to grey with time. The combusted powders were then placed in a tube furnace at 550 °C for 6 hours. None of the PEPF syntheses yielded phase-pure pyrochlores. It should be noted that it is very difficult to accurately calculate ϕ when PVA is used. This is because the molecular weight of the polymer is an estimated value between 9000 and 10000 g/mol. Furthermore, the polymer is said to be only 80% hydrolysed, adding further uncertainty since only 80% of monomers contain the -OH group. To obtain the amount of moles of monomer added, one then has to use an average molecular weight of the polymer, divided by the molecular weight of the monomer, which will give the amount of monomers present. The valence of PVA was calculated as follows: PVA (monomer):$(2C \times -4) + (4H \times -1) + (1O \times 2) = -6$

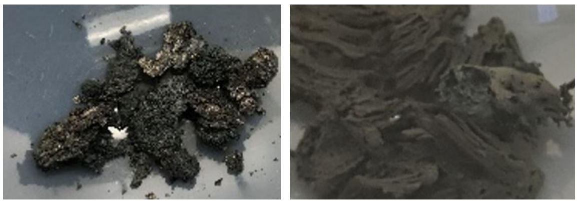

Figure S4: alanine (left) glycine (right)

S4. Combustion/calcination procedures

The gel to be combusted can be either fully dried or partially dried. This affects the appearance of the produced product (Figure S5). The dried gel produces finely separated particles, whereas the wet gel produces a fluffy combusted product.

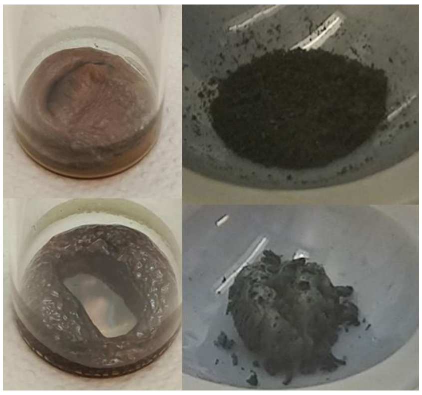

Figure S5: Dry gel(top) and wet gel (bottom) before (left) and after (right) combustion

S5. Electrochemistry

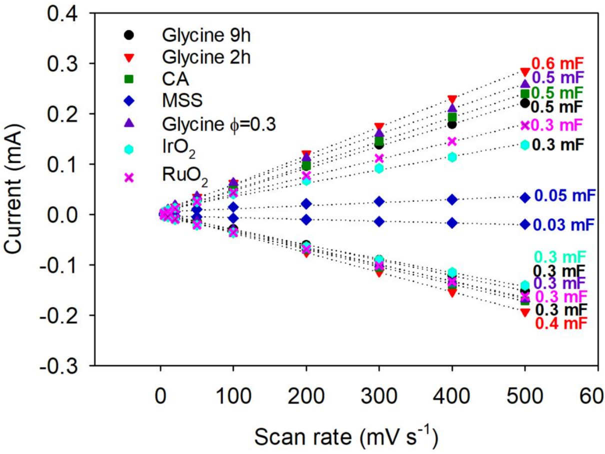

Figure S6: Current versus scan-rate plots for the forward and backward scans of each of the pyrochlores where the slope yields the value of the double layer capacitance.

Figure S6 displays plots used to obtain the double layer capacitance for each electrocatalyst, which can in turn be used to obtain ECSA by dividing by a specific capacitance value.[3] Cyclic voltammograms obtained during the down cycling step (Table 1) can be seen in Figure S7.

In Figure 18 in the main text, the LSVs normalised in terms of active area is displayed. Figure S8 shows the geometrically normalised LSVs. The limited straight-line portions of the polarisation curves provide one with the Tafel slope (Figure S10). However, it is also possible to fit the entire curve as described by Reksten *et al.*[4] (Figure S11). From these fits, the oxygen binding energy (E_O) can be obtained. These values are

3.459 eV, 3.439 eV, 3.427 eV, 3.403 eV and 3.469 eV for the glycine 9h, glycine 2h, CA, MSS and glycine ϕ=0.3 samples, respectively. The glycine ϕ=0.3 sample has the highest E_O value and MSS the lowest, in accordance with their activities outlined in Figures 18 and S8. The E_O values for RuO_2 and IrO_2 are 3.382 eV and 3.555 eV, respectively.

Furthermore, Figure S12 shows the LSVs obtained initially, after 100 CVs between 1.4-1.6 V, after 100 CVs between 0.2 and 1.3 V (down cycling) and after 700 CVs between 1.4-1.6 V. The CVs are shown in Figure S13, showing the first, 50th and 100th cycles of the first 100 stability CVs and the first, 250th and 700th cycles of the second 700 stability CVs. In addition, Figure S14 shows 4 minute potential holds of the pyrochlores at at 1.57, 1.58, a.59 and 1.6 V. Figure S14 indicates that the pyrochlores are not stable in this potential range, as the current decreases with time at each of these respective potentials.

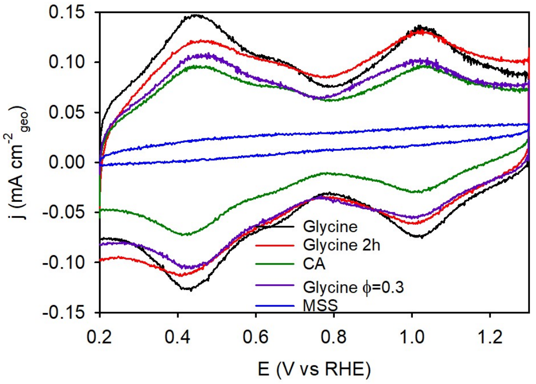

Figure S7: The 50th cyclic voltammograms of each pyrochlore during the down cycling step in the electrochemical procedure.

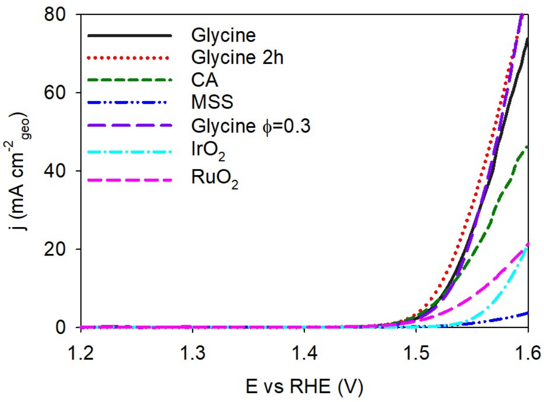

Figure S8: LSVs (geometric area normalised) of $Y_2Ru_2O_7$ synthesised with the combustion synthesis method under different conditions as well as the citric acid method. The LSVs for reference RuO_2 and IrO_2 are also included.

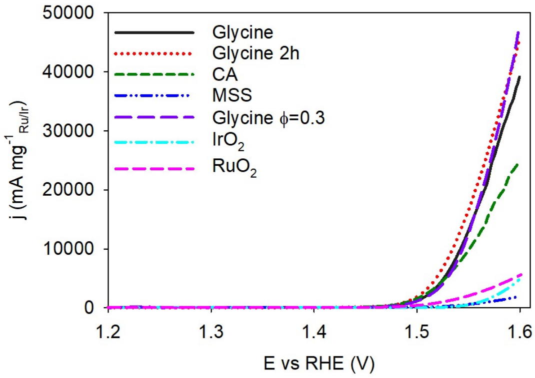

Figure S9: LSVs (normalised with respect to the mass of Ru/Ir) of $Y_2Ru_2O_7$ synthesised with the combustion synthesis method under different conditions as well as the citric acid method. The LSVs for reference RuO_2 and IrO_2 are also included.

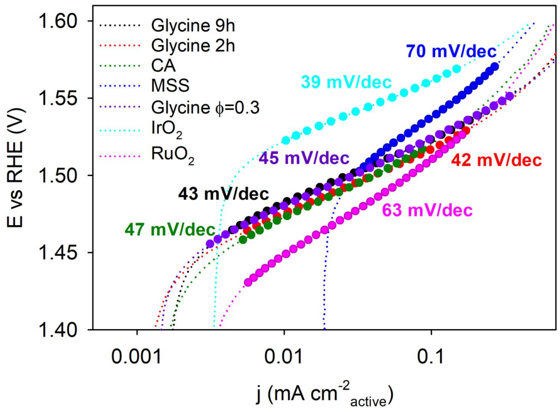

Figure S10: Logarithmic plots of the current density obtained from an LSV at 5 mV s^{-1} in 0.5 M H_2SO_4 of $Y_2Ru_2O_7$ synthesised under different conditions. The plots for reference RuO_2 and IrO_2 are also included. The straight line portions used to obtain the Tafel slopes are indicated.

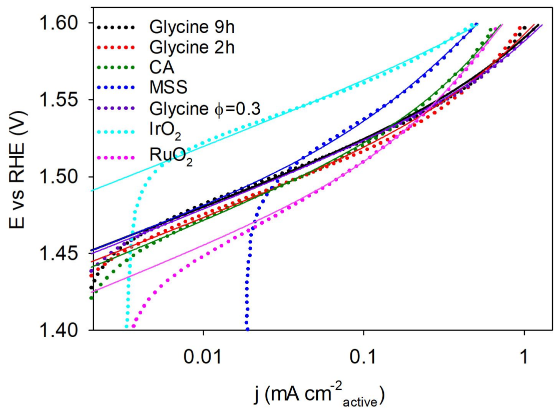

Figure S11: Polarisation curves fitted to the cc mechanism outlined by Reksten *et al.*[4] The curves are obtained from an LSV at 5 mV s^{-1} in 0.5 M H_2SO_4 of $Y_2Ru_2O_7$ synthesised under different conditions. The plots for reference RuO_2 and IrO_2 are also included.

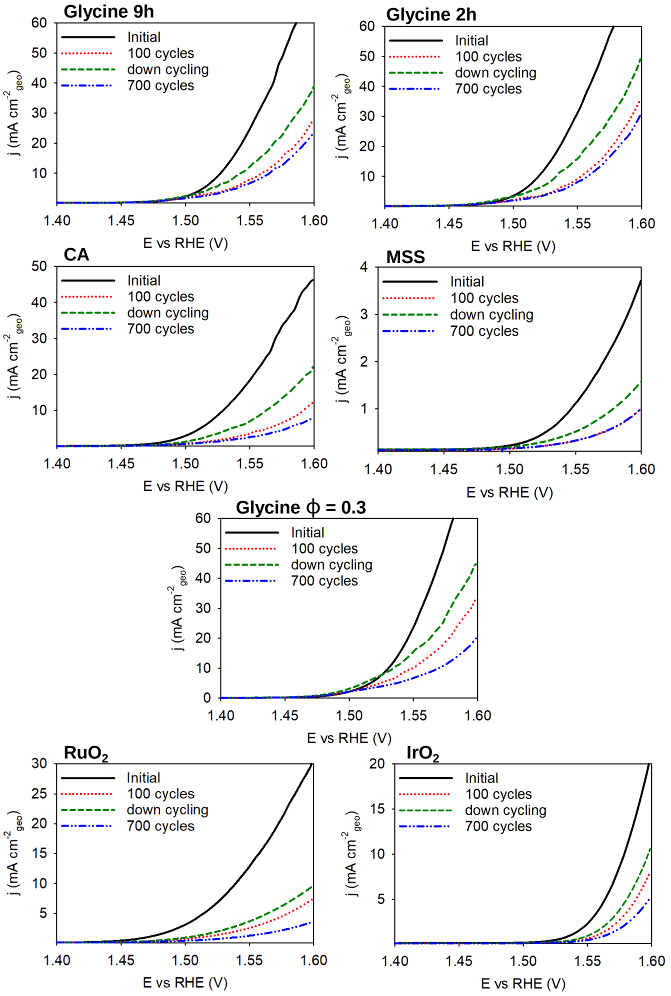

Figure S12: LSVs recorded before and after stability tests, and regenerative down cycling, on each of the pyrochlores prepared by altering synthesis parameters.

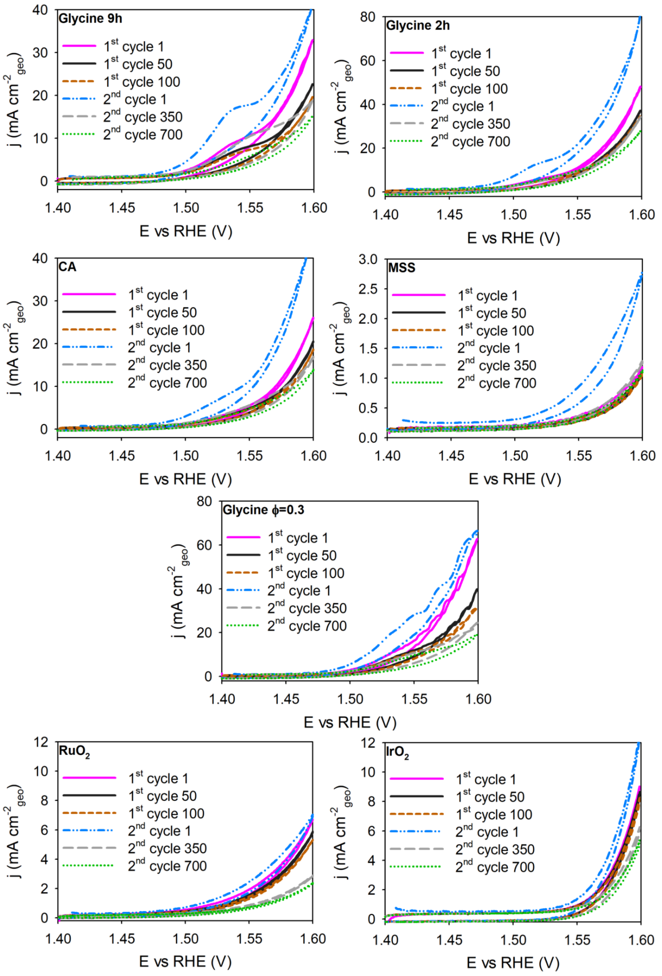

Figure S13: Cyclic voltammograms recorded duringf the stability cycling protocols. 1st refers to the first 100 CVs and 2nd refers to the second 700 recorded after regenerating the catalyst by down cycling.

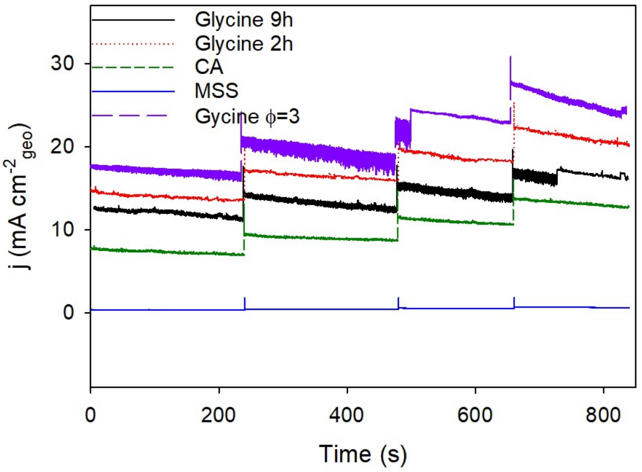

Figure S14: Four-minute potential holds at 1.57, 1.58, 1.59 and 1.6 V in 0.5 M H_2SO_4.

S6. Physical characterisation

S6.1. Raman spectroscopy

From the Raman spectra in Figure S15, it can be seen that the E_g (300 cm^{-1}), T_{2g} (400 cm^{-1} and 700 cm^{-1}) and A_{1g} (500 cm^{-1}) fundamental modes of the ideal pyrochlore (according to group theory) are present for all calcined samples.[5][6] This is further evidence that pyrochlore phases were successfully synthesised. The spectra are also in good agreement with Raman spectra for $Y_2Ru_2O_7$ reported in literature. For example, peaks at 315 (E_g), 410 (T_{2g}) and 510 cm^{-1} (A_{1g}) have been observed for $Y_2Ru_2O_7$ by Bae *et al.*[7] Raman modes are sensitive to changes in the lattice parameter and the peaks will shift as it increases or decreases.[8] Specifically, the position of the A_{1g} peak at ca. 500 cm^{-1} is often used to determine if structural changes are present in these pyrochlores.[8][9][10] The A_{1g} peaks of the sample calcined for 2 hours at 1000 °C (both with and without MSS) is shifted very slightly to the right (to higher frequencies), which could be indicative of a decreased lattice parameter for these samples. However, since no major peak shifts are observed, it can be assumed that the structures for all samples are similar. In addition to the pyrochlores, we also included the Raman spectrum of the oxides after combustion but before calcination (the yellow plot in Figure S15). This spectrum contains two visible peaks, one at around 370 cm^{-1} and one that is at the same position (700 cm^{-1}) as the peak corresponding to the T_{2g} mode of the pyrochlores. Interestingly, the pyrochlore prepared with citric acid has the clearest/ largest peak at this position.

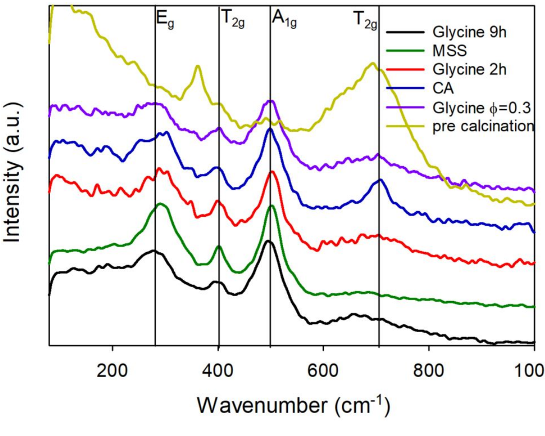

Figure S15: Raman spectra of yttrium ruthenate pyrochlores prepared under different synthesis conditions after and before calcination.

S6.2. XPS

Figure S16 showds the Y 3d XPS spectra for each of the pyrochlores. The peak postions correspond well to that reported for these pyrochlores in previous work.[11]

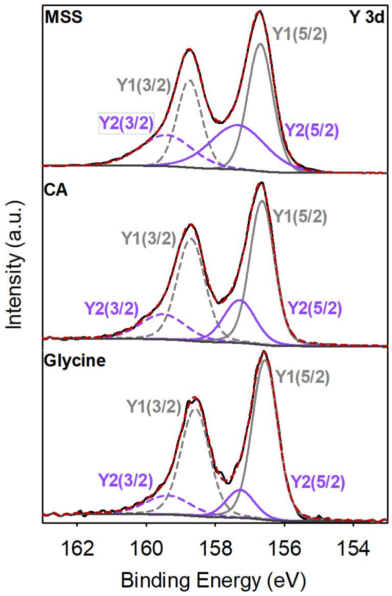

Figure S16: Y 3d XPS spectra for pyrochlores prepared when citric acid and glycine (9 hour calcination as well as 2 hours in molten salts) are used respectively.

S6.3. XAS

In Figure S17 the EXAFS spectra of the Ru edge of the pyrochlores are shown before any processing in Excurve software. We include this figure for easier comparison with other papers on pyrochlores that do not employ fitting. The fitted spectra can be seen in Figure 16 in the main text, and the fit results are displayed in Tables S1 and S2 for the first and second shells respectively.

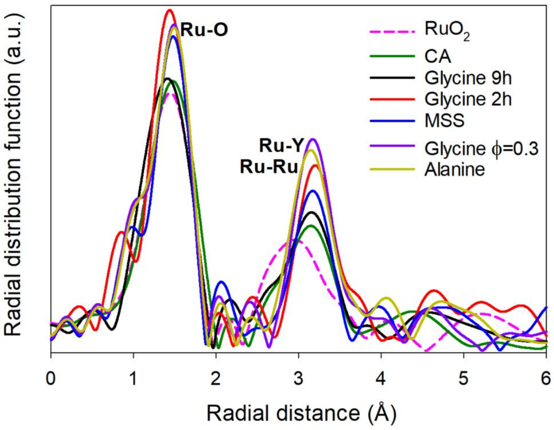

Figure S17: Fourier transformed EXAFS spectra of the Ru edge for pyrochlores prepared by different synthesis parameters and RuO_2 before fitting in Excurve.

Table S1: Fitting results for the Ru-O shell

Sample	R	N	E_F	A
CA	1.99±0.008	5.2±0.8	-1.4±1.2	0.0005
Gly 9h	2.00±0.012	6.66±1.2	-2.2±1.4	0.008
Gly 2h	1.98±0.011	6.58±1.1	0.39±1.4	0.005
MSS	1.99±0.012	5.8±1.2	0.59±1.7	0.001
Gly 0.3	1.99±0.008	6.4±0.8	-0.78±1.0	0.004
Alanine	1.99±0.007	6.5±0.8	-0.6±1.0	0.005

Table S2: Fitting results for the Ru-Ru/Y shell

Sample	R	N	E_F	A
CA	3.60±0.008	5.2±2.2	-1.4±1.2	0.0003
Gly 9h	3.63±0.014	7.63±4.5	-2.2±1.4	0.008
Gly 2h	3.61±0.010	6.84±3.9	0.39±1.4	0.005
MSS	3.61±0.017	9.8±7.6	0.59±1.7	0.001
Gly 0.3	3.61±0.008	6.3±2.6	-0.78±1.0	0.004
Alanine	3.60±0.007	8.6±2.7	-0.6±1.0	0.005

S6.4. EDS

In this section, the EDS mapping of yttrium and ruthenium in each pyrochlore (Figures S18-S21) is shown. It can be seen that the elements are evenly distributed without obvious phase separation. Furthermore, we also include the mapping of the uncalcined combusted sample (Figure S22), which also shows an even distribution of the elements. In addition, spot/area analysis results can be seen in Figure S23.

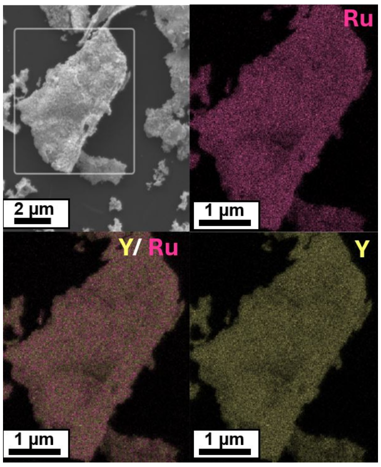

Figure S18: EDS mapping of the pyrochlore prepared with citric acid as fuel.

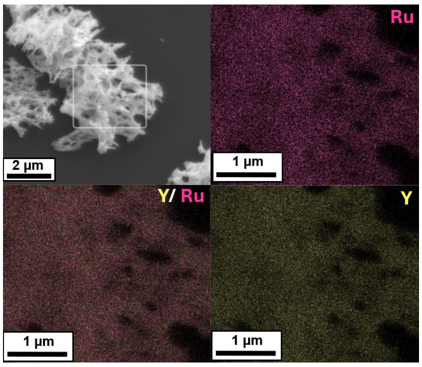

Figure S19: EDS mapping of the pyrochlore prepared with glycine as fuel and calcined for 9 hours.

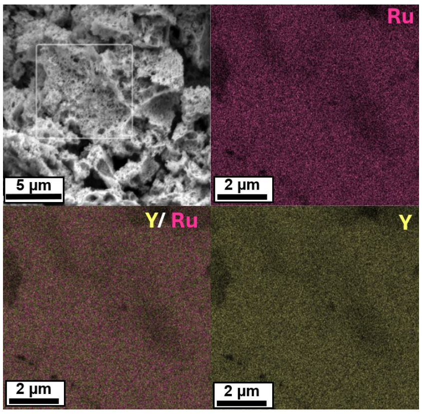

Figure S20: EDS mapping of the pyrochlore prepared with glycine as fuel and calcined for 2 hours.

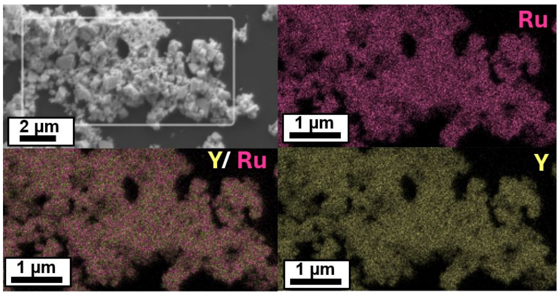

Figure S21: EDS mapping of the pyrochlore prepared with glycine as fuel and calcined for 2 hours in a molten salt mixtue.

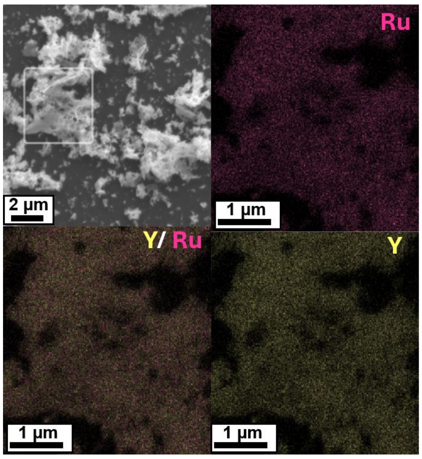

Figure S22: EDS mapping of the pyrochlore prepared with glycine as fuel right after combustion and no calcination.

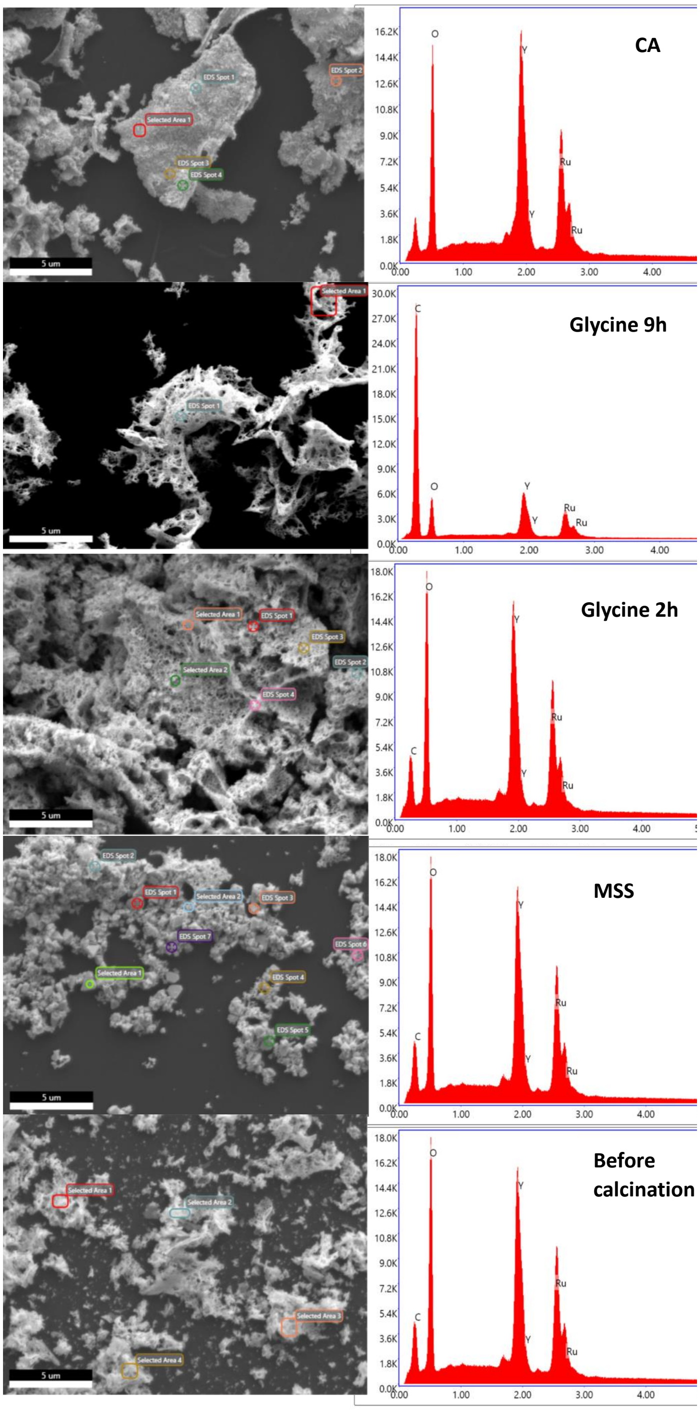

Figure S23: EDS point/area results for each sample.

S6.5. BET

The BET measurement curves of the samples prepared by the combustion synthesis method and the MSS method are shown in Figures S24 and S25, respectively. The BET surface specific area of the particles prepared by the combustion synthesis method was 18.4925±0.2087 $m^2\ g^{-1}$, and that of the samples prepared with an MSS step was determined to be 1.8180 ± 0.1102 $m^2\ g^{-1}$, which is ten times less than that of the samples prepared by the combustion method. The pore size distributions shown in the insets (Figures S24 and S25) were calculated with desorption data using the Barret–Joyner–Halenda (BJH) model. The total pore volumes of the combustion and MSS samples were 0.005937 $cm^3\ g^{-1}$ and 0.000517 $cm^3\ g^{-1}$, respectively. Both samples contain a majority of pores around 130 nm in size, buth the combustion sample has a 10 times higher pore volume.

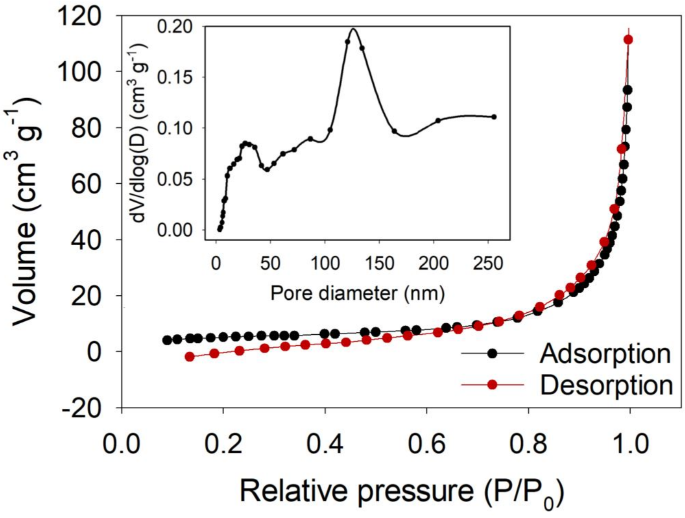

Figure S24: BET measurement curves and pore size distribution of particles prepared by the combustion synthesis method.

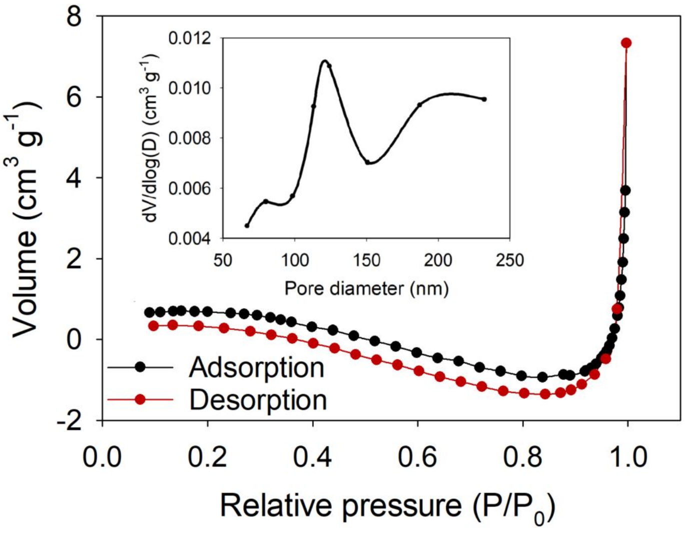

Figure S25: BET measurement curves and pore size distribution of particles prepared by the MSS synthesis method.

S7. Theory: The oxygen balance (OB)

Hwang *et al.* uses a simplified reaction equation when complete combustion is assumed to express the OB.[12] The same approach can be used to describe the reaction equation and OB for synthesising $Y_2Ru_2O_7$ in the equations below. A few assumptions need to be made. Firstly, for the $Ru(NO)(NO_3)_x(OH)_y$ (x+y=3) precursor, we need to assume values for x and y, to which we assign both to 1.5.

$$2Y(NO_3)_3 \cdot 6H_2O + 2Ru(NO)(NO_3)_{1.5}(OH)_{1.5} + \Psi NH_2CH_2COOH + \kappa NH_4NO_3 \xrightarrow{mixing,dehydration} Y_2Ru_2C_{2\Psi}H_{3+5\Psi+4\kappa}N_{11+\Psi+2\kappa}O_{32+2\Psi+3\kappa} \xrightarrow{combustion} Y_2Ru_2O_7 + 2\Psi CO_2 + (1.5 + \frac{5\Psi}{2} + 2\kappa)H_2O + (5.5 + \frac{\Psi}{2} + \kappa)N_2 + (11.75 - \frac{9}{4}\Psi + \frac{\kappa}{2})O_2 \tag{1}$$

Herewith, $(18.75 + \frac{1}{2}\Psi + \frac{7}{2}\kappa)$ moles of gas is produced and the OB value can be expressed as[12]:

$$OB(\%) = \frac{AW_{oxygen}}{FW_{mixture}}(23.5 - \frac{9\Psi}{2} + \kappa) \times 100\% \tag{2}$$

where AW_{oxygen} is the atomic weight of oxygen, $FW_{mixture}$ is the formula weight of the mixture and the OB can be adjusted by varying Ψ and κ.[12] If the variables are adjusted such that OB<0 (fuel-rich)or OB>0 (fuel-lean), then excess oxygen is needed for the combustion or excess oxygen is present in the reactant mixture, respectively. If the OB is zero, the mixture is said to be stoichiometric and all of the nitrates in the mixture will react exactly to oxidize glycine equivalently.[12]