

## Exploitation of Bulk and Surface Exsolution in Perovskites Oxide for Hydrogen Production and Power Generation

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### Introduction

Exsolution entails the in-situ growth of catalytically active nanoparticles directly from an oxide-metal solid solution (perovskite) lattice.<sup>1</sup> The exsolution process has been advantageous in developing solid oxide cells for hydrogen production or power generation, but not necessarily for both simultaneously, which would be required for reversible solid oxide cells (RSOC).<sup>2</sup> RSOC could address renewable intermittency by working as an electrolytic cell for hydrogen production and, in reverse mode, as a fuel cell for power generation.<sup>3</sup> For example, exsolution enhances surface nanoparticles' stability and resilience to agglomeration and deactivation, while bulk exsolution can enhance conductivity.<sup>4</sup> Additional functionalities such as high electronic and ionic conductivity and high catalytic activity must be maintained for RSOC when switching between electrolysis and fuel cell mode.<sup>3</sup> Here, we seek to develop new perovskite materials that fulfil these requirements, using both surface and bulk exsolution to achieve this. The target compositions would belong to a family of A-site deficient perovskite with a stoichiometric composition such as  $(\text{Sr,Ca})_{1-x}(\text{Ti,Fe,Ni})\text{O}_3$ . Such A-site deficiencies are known for their ability to drive B-site exsolution while attempting to revert the perovskite to a defect-free or stable  $\text{ABO}_3$  stoichiometry.<sup>1,5</sup> To this end, we examine the parameters related to synthesising such new perovskite materials in this work. The thermogravimetry analysis (TGA) result revealed  $\text{Fe}_2\text{O}_3$ , NiO, and CaO as the decomposition products from three precursors. These decomposition products (oxides) could combine with  $\text{SrCO}_3$  and  $\text{TiO}_2$  to form the desired A-site deficient perovskite.<sup>1,5</sup> The scanning electron microscopy (SEM) result has revealed the morphologies of the respective precursor materials. It could be used to study the effect of such parameters on the resulting perovskite microstructure and the synthesis reaction. Therefore, this study's result has given insight into the need to properly understand precursor materials before their selection for a given perovskite synthesis.

### Materials and Methods

Five potential precursor materials,  $\text{Fe}(\text{NO}_2)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{TiO}_2$ , were studied at the current stage of this research. The materials were characterised by thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) to obtain information about their thermal stability, decomposition temperature, decomposition products, composition, and morphology. A Netzsch STA 449F3, DSC/TG equipment and Hitachi S3700 SEM equipment were used for the TGA and SEM analysis. The TGA was run at the temperature range of 30 - 550 °C for  $\text{Fe}(\text{NO}_2)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and 30 - 950 °C for  $\text{CaCO}_3$  and  $\text{TiO}_2$ , at a heating rate of 10 °C/min.

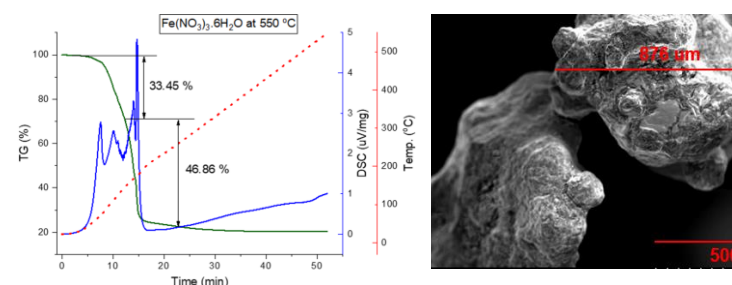
### Results and Discussion

Table 1 summarises the significant results obtained from the study. It was observed that  $\text{Fe}(\text{NO}_2)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{CaCO}_3$ , respectively, decomposed into  $\text{Fe}_2\text{O}_3$ , NiO, and CaO within the decomposition temperature ranges obtained. Figure 1 shows a TG curve, DSC curve and temperature response for  $\text{Fe}(\text{NO}_2)_3 \cdot 9\text{H}_2\text{O}$  plotted as a function of time, while Figure 2 shows the SEM image of  $\text{Fe}(\text{NO}_2)_3 \cdot 9\text{H}_2\text{O}$ .

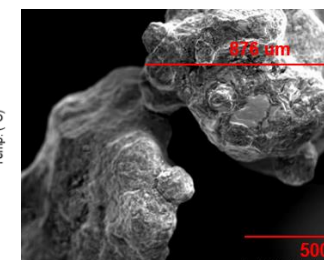
As presented in Table 1, while the decomposition of  $\text{Fe}(\text{NO}_2)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{CaCO}_3$  were observed within the analysis temperature ranges, the TG curve of  $\text{TiO}_2$  (Figure 1) predicted only minimal loss in mass. Such loss in mass in the  $\text{TiO}_2$  sample analysed cannot be linked to the decomposition effect. This shows  $\text{TiO}_2$  is stable over the temperature range and the test period. The absence of any exothermic peak in the DSC curve of Figure 1 also pointed out that no change in phase occurred in the  $\text{TiO}_2$  throughout the analysis period. The SEM image (Figure 2) shows that  $\text{Fe}(\text{NO}_2)_3 \cdot 9\text{H}_2\text{O}$  particles possess rough surfaces and irregular shapes. This, with the morphology of other precursor particles, may significantly influence the reaction during the perovskite synthesis. Therefore, knowing the impact of some synthesis processes on such parameters can guide the selection of a synthesis route for the perovskite material.

**Table 1.** Summary of key findings from the TGA of the four precursors studied

Precursor Material	Decomposition Temperature Range (°C)	Decomposition Stages	Decomposition Product
$\text{Fe}(\text{NO}_2)_3 \cdot 9\text{H}_2\text{O}$	50 - 400	Two stages	$\text{Fe}_2\text{O}_3$
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	56 - 573	Two-stage	NiO
$\text{CaCO}_3$	600 - 850	Single stage	CaO
$\text{TiO}_2$	-	-	-



**Figure 1.** A TG curve, DSC curve, and temperature response for  $\text{Fe}(\text{NO}_2)_3 \cdot 9\text{H}_2\text{O}$



**Figure 2.** The SEM image of  $\text{Fe}(\text{NO}_2)_3 \cdot 9\text{H}_2\text{O}$

### Significance

Achieving on-demand hydrogen and electricity production will require RSOCs that can start and switch between electrolytic and fuel cell modes as fast as possible. Such RSOCs must be fabricated from perovskite materials that fulfil the demanding electrochemical functionalities, hence the need to exploit the potentials of A-site deficient perovskite to be developed in this research. The results obtained have given helpful information that will guide the development of the synthesis route for the perovskite material.

### References

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