Experimental Report

03/10/2014

Proposal:	**5-22-724**	**Council:**	10/2012

Title: In situ studies of Redox Exsolution in Perovskites

This proposal is a new proposal

Researh Area: Materials

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Samples: Sr.4La.4Ti.94M.06O3-y M=Ni,Fe,Ce

Instrument	Req. Days	All. Days	From	To
D2B	3	3	01/07/2013	04/07/2013

Abstract:

Surfaces decorated with nanoparticles of catalytically active metals hold considerable promise in catalytic and electrochemical applications, including fuel cells. We have recently discovered that through control of defect chemistry we can fabricate intricately decorated surfaces that seem to show enhanced stability, probably due to some degree of surface anchorage. Here we wish to utilise neutron powder diffraction to study the growth of such structures, seeking to probe the growth mechanism, the chemical and structural nature of the nanoparticles and to determine if there is a direct interaction between the substrate and exsolute during the different growth stages.

In Situ Studies of Redox Exsolution in Perovskites

George Carins, Dragos Neagu, Emmanuelle Suard, John Irvine

1 Introduction

An experiment *In situ studies of redox exsolution in perovskites* was performed at the D2B diffractometer, Institut Laue-Langevin. Strontium titanate-type compounds with known with known nano-catalyst exsolution capabilities were studied. Of interest was the nature of exsoluted nanoparticles and their anchoring to the bulk material as well as the structural transformation of the parent perovskite.

2 Experimental

Three compositions of A-site deficient perovskites were synthesised using standard solid synthesis techniques:

$La_{0.52}Sr_{0.28}Ni_{0.06}Ti_{0.94}O_3$ (LSNT)
$La_{0.49}Sr_{0.31}Fe_{0.03}Ni_{0.03}Ti_{0.94}O_3$ (LSFNT)
$La_{0.8}Ce_{0.1}Ni_{0.4}Ti_{0.6}O_3$ (LCNT)

Precursors of metal oxides or carbonates were dried and weighed in required amounts for desired stoichiometries. Precursors were then mixed and calcined at 1000°C for 5 hours. Mixtures were ball milled, pressed and fired at 1410°C for 12 hours to form dense pellets. The pellets were crushed, ball milled, mixed with graphite pore former, pressed, and fired at 1395°C for 6 hours to form $\approx$ 8mm diameter, $\approx$ 10mm tall porous pellets. 5 pellets of each composition were produced. 2 pellets of each composition were reduced in 5%H_2/Ar at 920°C for 20 hours prior to scanning in the D2B diffractometer.

When scanning, two pellets of the composition under test were mounted within a quartz vial and suspended in a vacuum furnace (except the LSFNT in situ reduction where pellets were crushed before reduction). All runs were recorded in this environment. Gases were fed to the sample environment via a stainless tube within the quartz vial and the exhaust from the environment was fed through a paraffin bubbler to prevent back diffusion of air into the environment.

Pre-reduced samples of each composition were scanned at room temperature (RT) for 1 hour. Two pellets of LCNT were reduced in situ for 16 hours at 1000°C under 5%H2/Ar, following 2 hours each at 930°C and 950°C while scanning continuously. Three pellets of LSFNT were crushed and reduced in situ for 10 hours at 1000°C while scanning continuously.

Samples reduced in situ were later examined using a Jeol JSM-6700F field emmission SEM.

3 Results

Diffraction patterns of LCNT and LSFNT can be seen in 1 and 2. Patterns are shown of the pre-reduced samples and those of the in situ-reduced samples at different stages of the reduction processes. 1 shows clear evolution of a nickel metal phase in the LCNT system - the associated peaks are indicated with asterisks. These nickel metal peaks are most likely associated with exsolved nickel nanoparticles. The relative width of the peaks can be attributed to small crystallite size. The LSFNT diffraction patterns on the other hand show no obvious development of peaks that could be associated with nickel or iron metal. LSNT pellets were not reduced in situ.

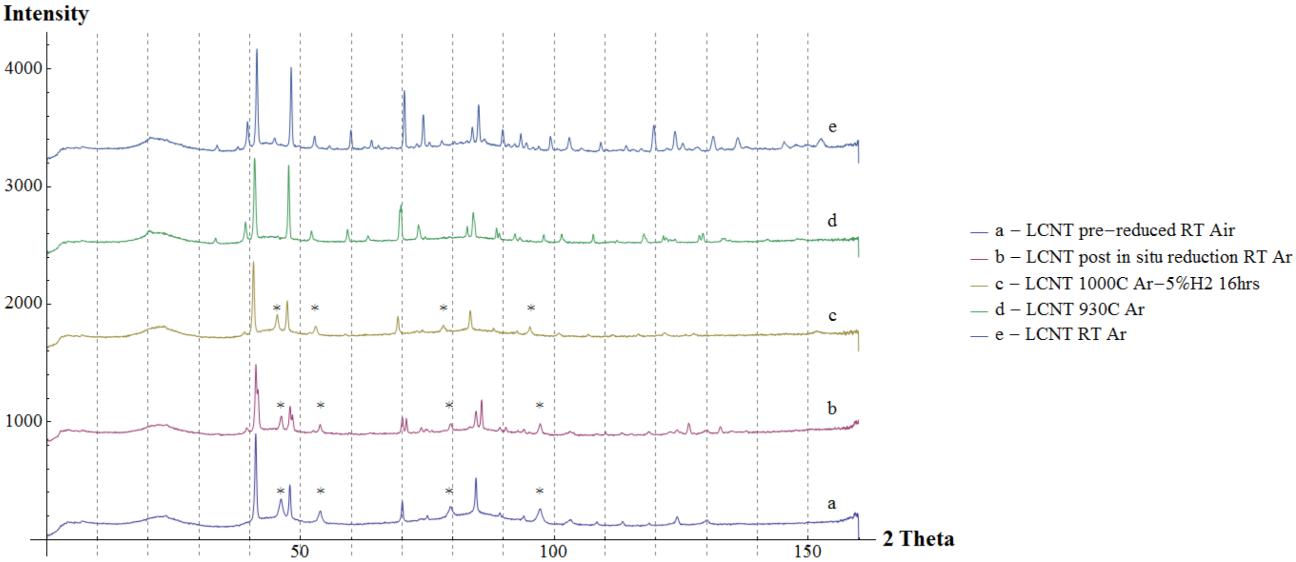


Figure 1: LCNT diffraction patterns - * indicate nickel metal peaks

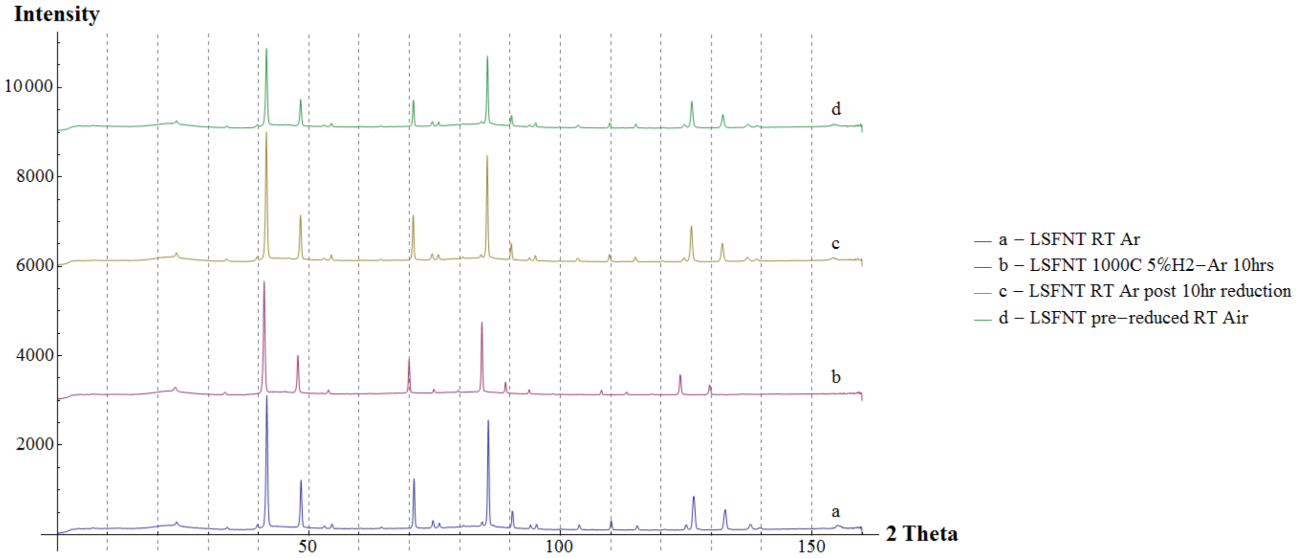


Figure 2: LSFNT diffraction patterns

Due to the lack of distinguishable metal phase derived diffraction peaks in the LSFNT patterns, analysis is focussed on the LCNT composition. The in situ-reduction data was binned into 20 minute datasets and sequential rietveld refinement was carried out using ”General Structure Analysis System” (GSAS) software. Key results of this are shown in 3. Here nickel fractional atomic occupancy within the perovskite lattice is plotted with nickel metal (nanoparticle) phase fraction of diffracted intensities. Each point represents refinement of a 20 minute dataset.

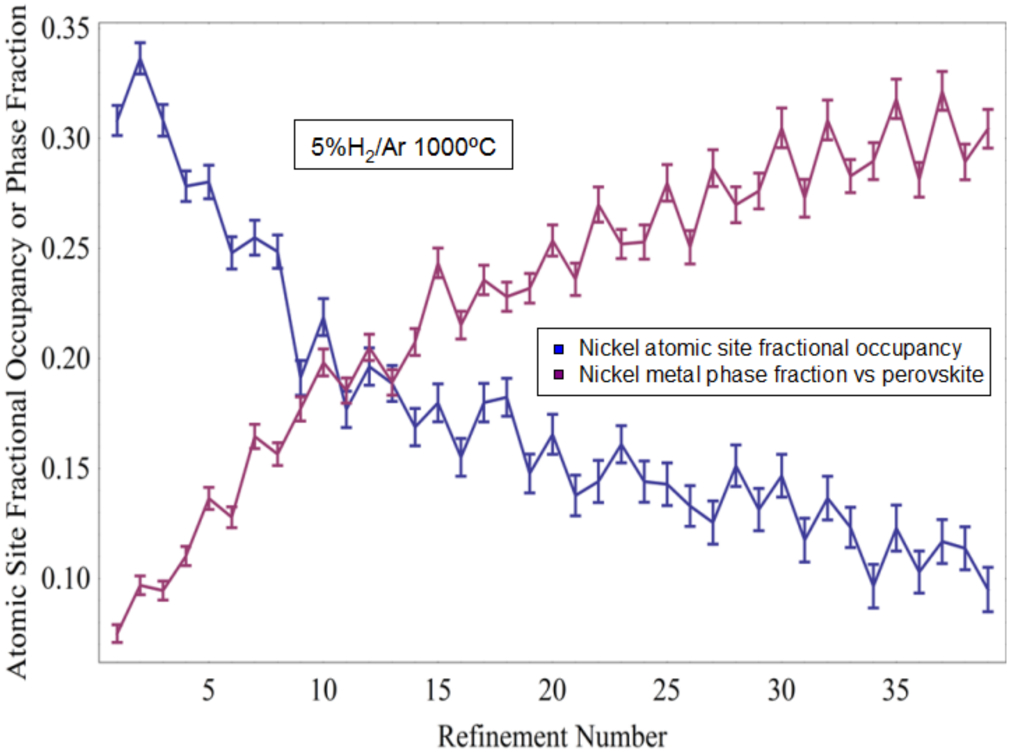
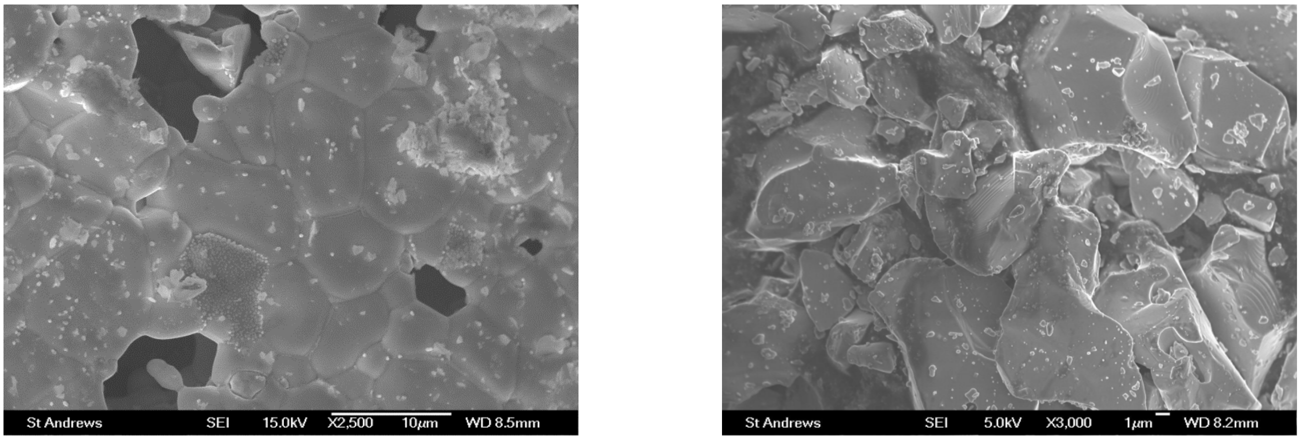


Figure 3: Nickel atomic fractional occupancy and nickel metal phase fraction

Both the LCNT and LSFNT samples were examined using a SEM post in situ reduction. Micrographs of each sample are shown in 4. The LCNT sample shows evidence of surface nanoparticles in the 10 to 100 nm range distributed inhomogeneously, with areas of high density. The LSFNT sample shows only a limited number of nanoparticles.



(a) LCNT post in situ reduction

(b) LSFNT post in situ reduction

Figure 4: A figure with two subfigures

4 Conclusions

Three perovskite compositions were synthesised. Samples of LSNT, LCNT and LSFNT were pre reduced and scanned. Sample of LCNT and LSFNT were reduced in situ while being scanned. It has been shown that in the case of LSFNT, no clear metallic phase can be observed in the diffraction data, but in the case of LCNT nickel nanoparticles were profuse.

These compositions and particular analogues will be researched further as promising electrode materials for electrochemical applications and catalysis.