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Investigating Sweet Spot Imaging of Perovskite Catalysts Bearing Exsolved Active Nanoparticles

Maadhav Kothari[1], Andy Holwell[1] and John Irvine[2]

[1.] Carl Zeiss Microscopy Ltd, Cambridge, UK.
[2.] School of Chemistry, St Andrews University, St. Andrews, UK.

Platinum (Pt), generally dispersed on a solid oxide support, has been widely used for catalytic chemical reactions in automobile, chemical refining, and energy industries. During the reactions, Pt is exposed to severe conditions, e.g., high temperature events and impurities, that cause Pt agglomeration and poisoning, respectively, resulting in activity/stability losses. Perovskite materials are designed with Pt for significant catalytic properties through novel doping and exsolution methods1. In order to accurately determine the catalytic ability of Pt nanoparticles, it is important to understand the structure and morphology of nanoparticles. Typical scanning electron microscopy methods do not reveal the morphological characteristics of nanoparticles due to the lack of electron beam stability. Here we demonstrate imaging techniques employed to accurately determine particle size and morphology. This method can improve the catalytic analysis of Pt loading, size, dispersion, and active sites determination.

Recent advances in new energy and heterogenous catalytic materials have resulted in novel ceramics being produced for a wide array of applications such as fuel cells, autocatalysis, and chemical feedstock production2,3,4. One such material is non-stoichiometric A-site deficient perovskite, with a catalytically active metal doped on the B site. It is possible through controlled synthesis and reduction conditions to tailor the size and morphology of nanoparticles through emergence of the active metal cations. To study the distribution, size, shape and morphology, careful scanning electron microscopy (SEM) needs to be deployed. The perovskite ceramic sensitivity, non-conductive nature, and nanoparticle distribution on the reduced area results in a difficult to image surface. This can often result in nano decoration being missed altogether due to lack of material understanding and microscopic technique.

Often in industrial testing for autocatalysis, a pelletized and sieved sample is observed and tested. This can lead to significant imaging issues due in part to debris, carbonaceous deposits from catalytic testing, and fine static particulate matter that can significantly reduce the sharpness of a micrograph. Typically, a solution to nonconductive materials would be sputter coat with either Gold (Au), Platinum (Pt) or Carbon (C) or a combination of coats ranging from 20 nm to 5 µm thickness for ceramic type materials. This can be counterproductive as often coating can lead to a masking of nanoparticles and false identification of both nanoparticles and carbonaceous deposits. Another factor in correctly identifying nanoparticles and distribution is the ability of substrate ceramic to be coated and catalytically react with typical desorption/adsorption-based techniques to characterize active metal sites, rendering these methods ineffective. SEM image analysis of nanoparticles is therefore a major area of interest to determine activity, stability, dispersion, and morphological features. Electron beam sensitive materials often require additional expertise and knowledge of the SEM best practice imaging technique known as sweet spot imaging. Here we demonstrate analytical micrographs of nanoparticles emerging from reduced Platinum containing A-site deficient perovskite noted as Pt+LCT.

A-site deficient perovskite Pt+LCT was synthesized using solid state synthesis and then reduced under 5% H2/Ar resulting in 0.5 wt% Pt. Emerged nanoparticles on the surface were studied using ZEISS

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Sigma 300, ZEISS Sigma 500, ZEISS Gemini 360 and ZEISS Gemini 560 SEM. For determining imaging conditions of Pt+LCT a range of apertures, working distance from beam pole and detector choice were selected to facilitate the best imaging practice (table 1). A range of microscope detectors was chosen within the ZEISS range, all using the Gemini column. For ceramic type materials and non-conductive materials it is best practice to image either at low keV (<5 keV) or variable pressure with a low working distance in relation to the pole piece. This is often different for individual microscopes, especially if the detectors and beam stability are variable. To find the best practice imaging for a certain material, a sweet spot analysis is required where various parameters are run through stepwise to find the best possible imaging conditions. By running through the test matrix in Table 1 the the ideal conditions for the Gemini series columns were found. It is clear that imaging ceramics at a higher keV (above 5 keV) damages the surface and sub-surface, resulting in degradation of the material within the chamber. An area of non-interest is initially advised to be selected for use with higher keV (5-20 keV). Once an optimal keV is chosen for the solution, tailoring the working distance for advanced resolution is advised to be under-taken as the next step. Finally, an approximate aperture is required between 5 µm of the selected aperture, e.g., 10 µm-25 µm should be experimented with to find the optimal conditions and increase the brilliance of imaging. Imaging snapshots can be taken with a rapid line scan initially to acquire the appropriate imaging settings in combination with drift correction. Further image corrections can be made post scanning with SmartSEM and SmartSEM Touch. Once imaging conditions have been selected, it is possible to observe regions of interest without damage to the selected area.

Table 1:

Microscope	keV imaged	Aperture µm	SE/Inlens	VP/BSE	Ideal condition
Sigma 300	10,5,3,1	50, 20, 15,10	SE & Inlens	VP-BSE 30 Pa	5 keV, 20 µm aperture, Inlens Working distance: 3.5 mm
Sigma 500	10,5,3,1	50, 20, 15,10	SE & Inlens	VP-BSE, Inlens	3 keV, 20 µm aperture, Inlens Working distance: 3-5 mm
Gemini 360	10,5,3,1	50, 20, 15,10	SE & Inlens	VP-BSE 20-30 Pa	1-3 keV 10-20 µm aperture, Inlens and VP-BSE 20 Pa Working distance: 4-7 mm
Gemini 560	10,5,3,1-<1	50, 20, 15,10	SE & Inlens	Inlens ESB	1-3 keV 10-20 µm aperture, Inlens and Inlens ESB Working distance: 2-7 mm

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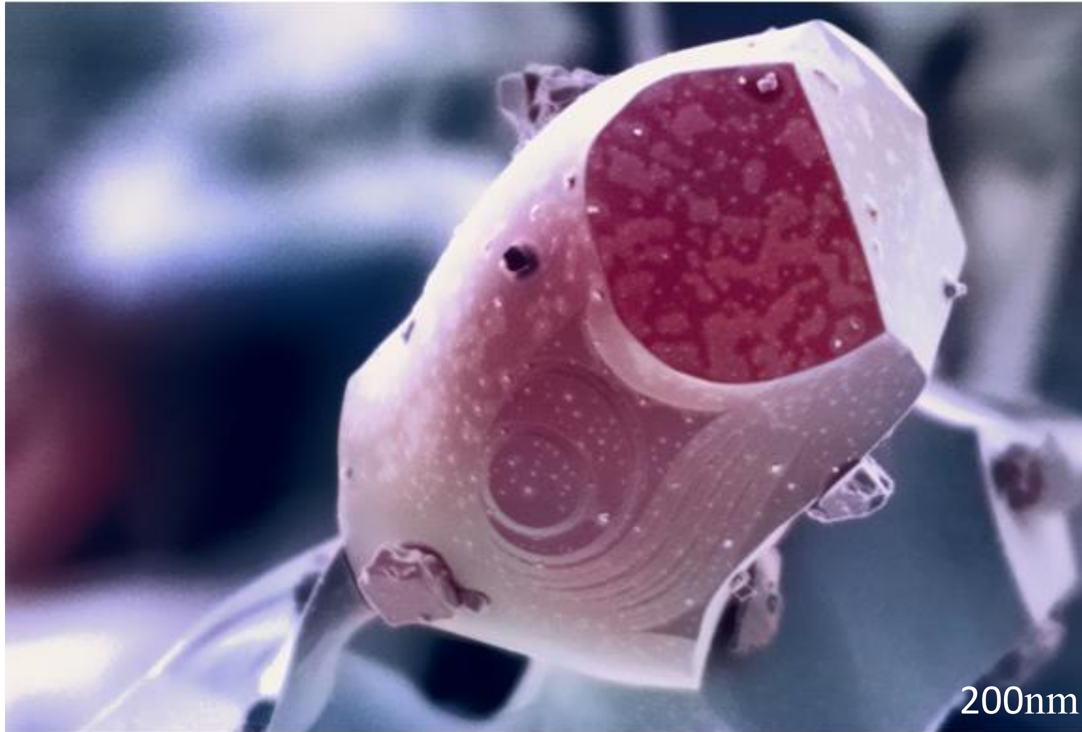
Figure 1: False colored micrograph of Pt nanoparticles decorating a ceramic Surface.



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