COMPARISONOF EXISTING TECHNIQUES TO MEASURE THE KINETIC FACTORS OF SOLID OXIDES TO THAT OF THE EMERGING TECHNIQUE OF THERMOGRAVIMETRIC ANALYSIS.

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ABSTRACT

Solid oxides with the ability to conduct oxygen are considered for utilization in applications in oxygen production and/or oxygen usage, for example as electrolytes in solid oxide fuel cells (SOFCs). The capability of solid oxides for these applications depend on how the oxides incorporate and conduct oxygen, which are determined by the surface exchange coefficient(K) and diffusion coefficient/diffusivity(D) of the solid oxide.

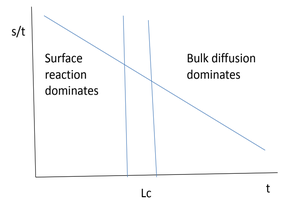
Existing techniques for measuring diffusivity (D) and surface exchange coefficient (K) like secondary ion mass spectrometry (SIMS), electrical conductivity relaxation (ECR) and isothermal isotopic exchange (IIE),are the main techniques used. These techniques have flaws which lead to complications and/or inaccuracies in measuring the oxygen rate limiting factor K. These flaws can be significantly reduced by an emerging technique. An emerging technique to evaluate the values of K is known as thermogravimetric analysis. The advantages with this technique supersede that of the established ones. Examples of the advantages of thermogravimetric analysis are that this technique is simpler to perform than the currently used techniques and the particles used are of nano- scale, hence the particle sizes are below the characteristic thickness (Lc) so good approximations of K are obtained.

Key Terms: Surface exchange coefficient, diffusivity, thermogravimetric analysis.

INTRODUCTION

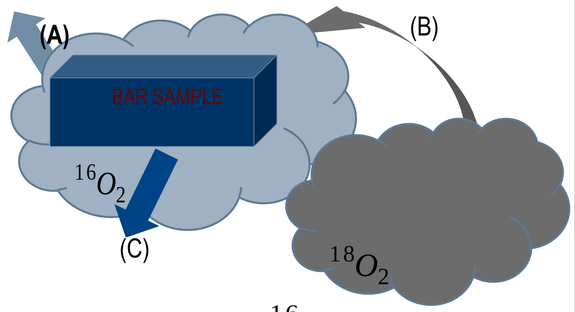
- The knowledge for solid oxides are important for determination of their use in technical ceramic.
- K is necessary for knowledge of the ease of oxygen flow through a material.
- SIMS and ECR techniques is used to measure surface exchange coefficient k.
- Samples are usually between 0.5mm-3mm thick.
- Thickness of the samples means k are being measured in bulk diffusion region using SIMS and ECR
- IIE is used in measuring K , IIE uses nano-sized powders hence good approximations of K are obtained.
- TGA is an excellent technique to measure K of nano-sized powder, no isotopic oxygen is required.

A PLOT SHOWING HOW SURFACE AREA VARIES WITH THICKNESS



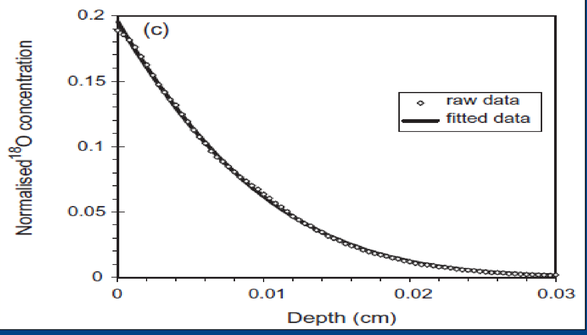
Lc is the characteristic thickness, for thicknesses below Lc surface reactions dominate and for thickness above Lc bulk diffusion dominates.

SIMS

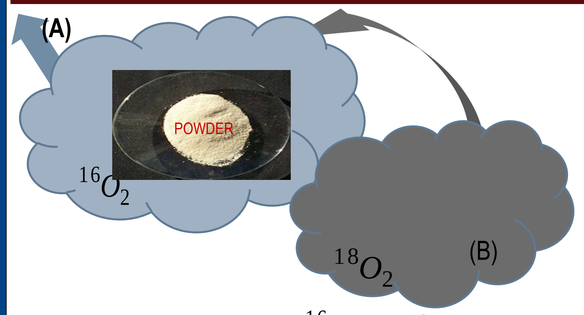


(A) SAMPLE EQUILIBRATED IN $^{16}O_2$, (B) $^{16}O_2$ IS REPLACED BY $^{18}O_2$, (C))THE SAMPLE IS THEN REMOVED FOR ANALYSIS.

A CONCENTRATION PLOT USING SIMS

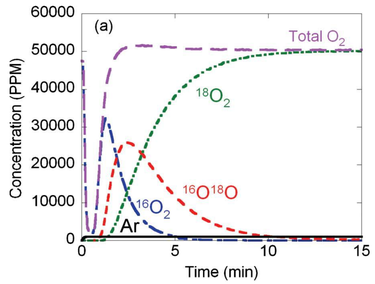


IIE

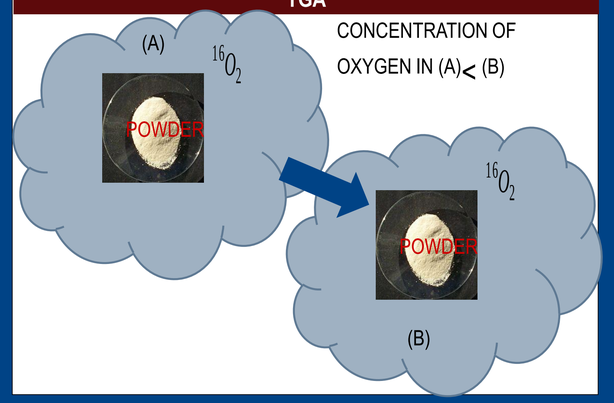


(A) SAMPLE EQUILIBRATED IN $^{16}O_2$, (B) $^{16}O_2$ IS SWITCHED OFF AND $^{18}O_2$ IS RELEASE INTO THE SYSTEM.

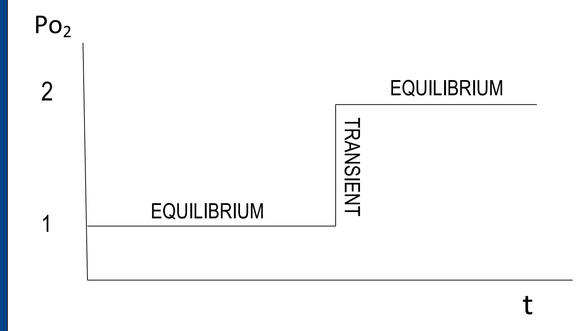
A PLOT OF CONVERSION OF OXYGEN IN THE LATTICE



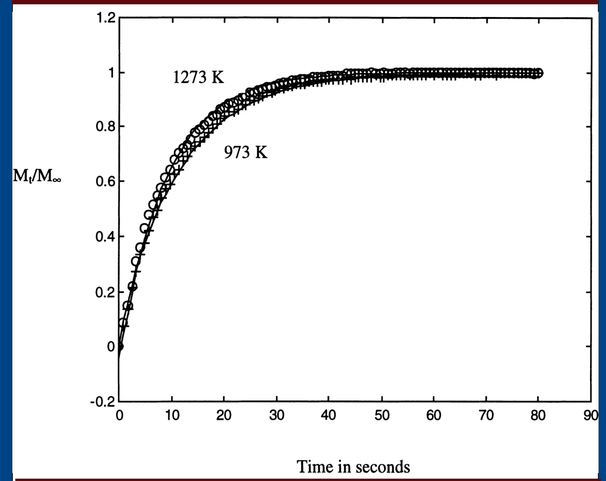
TGA



TRANSIENT RESPONSE FROM TGA



A PLOT OF MASS RATIO AGAINST TIME



CONCLUSION

When compared to the existing main techniques used for the determination of kinetic factors such as surface exchange coefficient, TGA is assured to give better results. Due to the fact that TGA uses powdered samples of with particles of the order of nano-sizes it is certain that surface reactions dominate the kinetics. The thickness of the particles used in SIMS and ECR makes it hard to isolate the surface kinetics. therefore K measured using these techniques are not valid. IIE is also a good technique to obtain K values, the drawback to IIE is that it requires the use of isotopic oxygen which makes it more expensive than TGA. TGA is the ideal technique to evaluate K since it use very small particles and does not depend on isotopic oxygen .