THERMOCHEMICAL INVESTIGATION OF THE EQUILIBRIUM OXYGEN
POTENTIAL OF RARE EARTH AND URANIA-RARE EARTH OXIDES
BY SOLID ELECTROLYTE COULOMETRY[x]

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## ABSTRACT

Solid state electrochemical cells have been used to measure
the interaction of non-stoichiometric oxides such as $CeO_{2-x}$,
$PrO_{1,5+x}$, $U_yRE_{1-y}O_{2+x}$ with $Ar-H_2-O_2$ gas mixtures. The thermo-
chemical interaction of these oxides with the carrier gas stream
was measured by an automatic continuous solid electrolyte coulo-
metric titration of the exchanged oxygen at temperatures of 1050
K to 1350 K in the narrow stoichiometric range.

## INTRODUCTION

Many oxide systems show a more.or less wide range of homoge-
neity. The thermal, electrical, optical, magnetic and other pro-
perties of such oxides depend from their stoichiometric composi-
tion. Small changes in stoichiometry may be relevant to these
composition-property relations. The real criterion for stability
of such oxide systems is  the minimization of free energy and it
is recomendable to consider the equilibrium diagram in $(G,T,x)$
space, where G is the free energy per atom and x the atom-frac-
tional composition. It has been emphasized, that many oxides have
such a narrow homogeneity range that different compositions can-
not be distinguished by classic chemical analysis. A useful me-
thod to investigate such systems is the thermogravimetric ana-
lysis in a controlled atmosphere. An alternativ procedure to in-
vestigate the thermochemical interaction of an oxide or other
materials in a carrier gas stream with a well defined oxygen po-
tential we have found to be the automatic continuous solid elec-
trolyte coulometric titration of the oxygen exchanged.

## MEASURING METHOD

The basic concept of the.solid state electrolyte cell applied
in this work is a four-electrode arrangement with porous platinum
layers on a zirconia-calcia solid electrolyte tube /1/. The first

electrode system is used for oxygen dosage or pumping according to the FARADAY's law and the second serves the open-circuit measuring of NERNST voltage. Main characteristics of the cell are:

    temperature of the potentiometric part of the cell    973 K
    temperature of dosing part of the cell    923 K
    nominal gas flow    6 1/h
    dosing current    0...20 mA
    concentration range of oxygen dosage    0...500 vpm

The device for measurement of solid-gas interaction is shown in fig. 1.
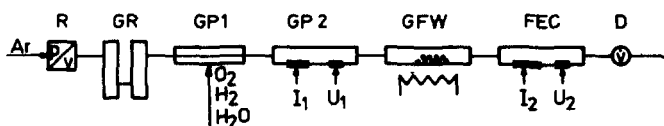


Fig. 1. Device for investigation of solid-gas interaction
        R, flow control; GR, gas purification; GP1, gas
        preparation with membrane; GP2, gas preparation
        and control with solid electrolyte cell; FEC,
        automatic solid electrolyte coulometric control
        of the gas; D, flow meter.

The purified steady state gas stream (Ar) is loaded with hydrogen, water vapour and/or oxygen after passing a thermostated diffusion line and controlled with a first solid electrolyte cell relating to oxygen potential. After reaction with the solid oxide investigated in a heated quarz tube the gas passes a second cell. The change of dosing current of this cell is equivalent to the exchanged amount of oxygen and stoichiometric composition, respectivily.

RESULTS

For analytical purposes this method was found to be very precise and standard deviations down to $x=\pm 0,0007$ have been reached. Thus, the solid electrolyte coulometry is recommended as a useful method independent of calibration /2/. The thermochemical interaction of above mentioned oxides with $Ar-H_2-H_2O$ and $Ar-O_2$ mixtures, respectivily, leads to the $\ln p_T - x$ plots, where $\ln p_T$ is

the equilibrium partial pressure of oxygen at the temperature T. Ranges of investigation applicated in this work are given in following table:

| supstance | temperature (K) | pressure (Pa) | x |
|-----------|-----------------|---------------|---|
| $UO_{2+x}$ | 1330 | $10^{-4}...10^{-13}$ | 0,1 |
| $CeO_{2-x}$ | 1050...1300 | $10^{-7}...10^{-9}$ | 0,02 |
| $PrO_{1,5+x}$ | 1000...1300 | $1 ...6$ | 0,02 |
| $U_{0,7}Ce_{0,3}O_{2\pm x}$ | 1050...1400 | $10^{-6}...10^{-10}$ | 0,01 |
| $U_{0,7}Pr_{0,3}O_{2\pm x}$ | 1050...1400 | $10^{-5}...10^{-10}$ | 0,01 |
| $U_{0,8}Gd_{0,2}O_{2-x}$ | 1030...1330 | $10^{-4}...10^{-14}$ | 0,005 |

An adequate fit of the plot of $\ln p_T$ against oxygen-metal ratio is found to be the equation

$$\ln p_T = \ln p_{x=0} + n \, \text{arsinh} \, \frac{x}{k} \, ,$$

where n is a constant, $\ln p_{x=0}$ and k are functions of temperature.

REFERENCES

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