The Electrochemical Evolution of O_2 on $NiCo_2O_4$ in ^{18}O-enriched KOH

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Summary Measurements of the incorporation of ^{18}O in an $NiCo_2O_4$ electrode show that during oxygen evolution in KOH solution an unstable surface oxide is formed with approximately one site per surface unit cell.

The evolution of oxygen on transition metal oxide anodes in alkaline solution may proceed *via* unstable, high oxidation states of the metal.[1,2] It is the purpose of this communication to describe a method to demonstrate this effect and to obtain an estimate of the number of sites at the electrode surface responsible for the evolution of oxygen

Oxygen was evolved on an $NiCo_2O_4$ electrode in KOH containing ^{18}O The kinetics of the subsequent evolution of ^{18}O from the electrode in unenriched KOH, measured by mass spectrometry, gave the number of sites on a particular electrode to be 8 8 × 10^{14} cm^{-2} which represents a ratio of the number of sites to the number of formula units in the catalyst of *ca* 0 1 This ratio was found for three similar electrodes and was independent of the current passed during evolution in normal alkali The time lapse between evolution in ^{18}O-enriched alkali and normal alkali was 5 min for most experiments No ^{18}O was detected in the evolved gas when an electrode was washed for 4 h in one experiment, or when an electrode was allowed to stand in air for 4 h after washing for 3 min The number of sites determined did not change when the evolution current in ^{18}O enriched alkali was raised from 500 to 1000 mA

An electrode of high surface area $NiCo_2O_4$ [29 m^2g^{-1} from B E T (Brunauer–Emmett–Teller) measurements] was prepared by dipping an 80 mesh nickel screen of geometric area 20 cm^2 into a solution of 1 mol dm^{-3} $Co(NO_3)_2$ $6H_2O$–0·5 mol dm^{-3} $Ni(NO_3)_2$ $6H_2O$ and decomposing the adhering solution in air at 300 °C Approximately five applications of the solution were required to give 7 to 10 mg of oxide per cm^2 of screen The electrode was then heated at 400 °C for 10 h *X*-ray examination of the oxide confirmed the spinel structure Oxygen was evolved at constant current (typically 500 mA for 30 min, 25 °C) in enriched alkali (5 mol dm^{-3} KOH, 5 atm% ^{18}O) on an $NiCo_2O_4$ electrode with Ni counter electrode The working electrode was washed and introduced into a second cell containing normal alkali, the anode compartment of which was connected *via* a variable bleed to a mass spectrometer (V G Micromass 12) After purging with argon, oxygen was evolved at constant current for a time while the peak heights of *m/e* 28, 32, 34, and 40 were measured The bleed rate into the mass spectrometer was adjusted to match the rate of oxygen evolution The fraction of ^{18}O atoms in the oxygen evolved at the electrode (x^*) was calculated, and allowance made for any residual oxygen from the air

The results of a typical experiment are given in the Figure, with those of a blank experiment in which an electrode was soaked in enriched alkali before washing According to the 'higher oxide' model[1] the rate of decomposition of oxide, which is equal to the rate of oxygen evolution, must be $iL/2F$ atoms s^{-1} (L is Avogadro's number, F is Faraday's constant) Thus, the rate of evolution of ^{18}O from the surface oxide is $iLx^*/2F$ atoms s^{-1} where x^* is the fraction of ^{18}O in the oxide The experimental points were fitted to an expression of the form $x^* = x^\circ + a \exp(-iL/2Fn_T\, t)$, where x° is the fraction of ^{18}O in normal alkali, a is a constant which depends on the time lag between the evolution of oxygen and its detection by the mass spectrometer and n_T is the total number of exchange sites on the electrode

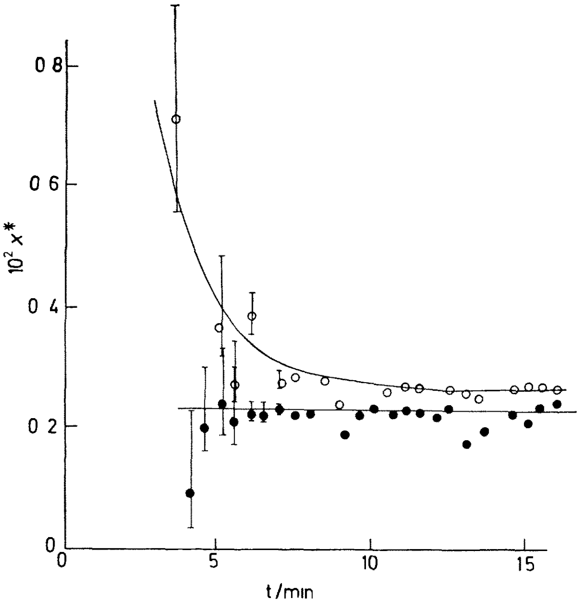

FIGURE The percentage of ^{18}O atoms evolved on an enriched $NiCo_2O_4$ electrode (10^2 x^*) in normal KOH as a function of time ○ = O_2 evolved in ^{18}O-enriched KOH at 500 mA for 30 min Washed 3 min total elapsed time 6 min before evolution in normal KOH at 250 mA ● = Blank experiment Electrode soaked in ^{18}O enriched KOH for 30 min Washed 3 min total elapsed time 5 min before evolution in normal KOH at 250 mA

It may be concluded that oxygen atoms from the electrolyte are incorporated into an $NiCo_2O_4$ electrode in some relatively unstable form possibly as a short-lived surface compound It is unlikely that rapid exchange with lattice oxygen occurs, as has been suggested by recent quantum mechanical calculations on TiO_2 and $SrTiO_3$ [3] The mean particle diameter of $NiCo_2O_4$ of specific surface area 29 m^2g^{-1} is 345 Å For a unit cell of edge 5 5 Å 10% of the unit cells are found at the surface Thus, from the values of n_T determined here there is approximately one exchange site per surface unit cell

It must be noted that a certain fraction of the sites are not used during steady state operation owing to bubble formation and the expulsion of electrolyte from pores in the catalyst [5] However, the above calculation reveals that oxygen is evolved through a surface complex This result is in contrast to recent coulometric studies of the formation of higher oxides on $NiCo_2O_4$ below the potential at which oxygen is evolved,[4] which concluded that the bulk of the oxide is transformed to a higher oxide during the reaction

The B E T surface area of the catalyst was measured by P Rasiyah of The City University, London

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