

The "Chameleon Surface"

A New Concept for a Solid State Reference Electrode

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ABSTRACT

A new concept for an "all solid state" reference half-cell for use in aqueous solutions based on mixed valent transition metal oxides is presented. XPS-surface analytical measurements demonstrate the adaptation of the surface chemistry to the chemistry of the solution ("Chameleon Surface"). Thus the driving force of the potential formation at the solid/liquid interface is significantly attenuated which may explain the electrochemically observed sub-Nernst sensitivities (~ 10 mV/pH).

PROBLEM AND CONCEPT

The ideal potentiometric reference electrode for use in aqueous solution is characterized by a well defined constant potential difference (ΔE) versus any aqueous solution independent of the ion activities therein.

A potential determining interaction between the electrode and some charged species in the solution is required to generate a stable potential drop. However, if the reaction is electrically reversible ΔE is expected to be dependent on the activities of the charged species involved. ΔE is then given by the Nernst equation,

$$\mu_{\text{solid}} / \mu_{\text{liquid}} = \exp \{-n \Delta E q / kT\}$$

which is a direct consequence of thermodynamics, i.e. equilibrium conditions. Reference electrodes can only operate at non-equilibrium but steady-state conditions.

Conventional reference electrodes consist of an electrode of the second kind connected to the solution via a liquid junction. There is an irreversible flow of cations and anions from the liquid part of the electrode into the probed solution.

The concept presented here is based on solids (mixed valent transition metal oxides) only. Irreversible corrosion reactions lead to an adaptation of the surface chemistry of the electrode to the chemistry of the solution ("Chameleon Surface"). Thus the driving force for potential generation becomes attenuated which can lead to very low sensitivities (~ 10 mV/pH) (see fig.1).

This concept was verified for La_xWO_3 and $\text{W}_{18}\text{O}_{49}$.

HALF CELL POTENTIAL MEASUREMENTS

Half cell potential measurements as a function of pH were carried out by titration of KOH/HCl to an air-saturated 0.1N KCl support electrolyte. All samples ($\text{W}_{18}\text{O}_{49}$ (fig.1) and La_xWO_3 ($x=0.06-0.2$)) exhibit the same principal behaviour: Constant but low pH sensitivity (~ 10 mV/pH) in the regime between pH 4 and pH 8 and significantly higher sensitivity beyond that limits.

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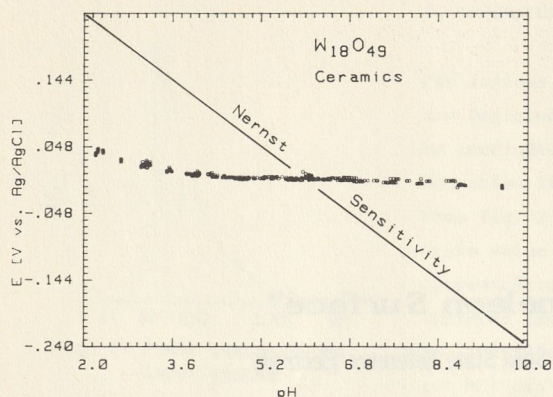


Fig.1
Half cell potential of $W_{18}O_{49}$ versus a KCL saturated Ag/AgCl-electrode ($T=30^{\circ}C$). The pH was recorded by a conventional pH-sensor. The pH-region shown was scanned several times (total measuring time: ca. 100 h).

XPS-SURFACE ANALYTICAL INVESTIGATIONS

The chemical and electrochemical reactions at the solid/liquid interface which account for the above described sub-Nernst behaviour have been investigated by XPS on a (111) face of a $La_{0.18}WO_3$ single crystal. Photoelectron spectroscopic experiments on surfaces after immersion in liquids have to be carried out very carefully. Contamination and subsequent surface reactions have to be avoided. Therefore the experiment was performed in the purified N_2 atmosphere of a glove box. After separation of the sample from the HCl/KOH solutions it has been transferred into the UHV chamber of the spectrometer in a UHV transport box. Details of the procedure will be described elsewhere. Three spectra of the W^{4f} doublet of surfaces with bulk composition and after immersion in solutions of pH 8.9 and pH 4.25 are shown in fig.2. Some preliminary results are:

- (1) After immersion in a solution of pH 8.9 the portion of W^{4+} is strongly increased compared to the bulk composition.
- (2) After immersion in more acidic solutions (e.g. pH 4.25) the W^{4+} portion is significantly decreased compared to (1) indicating an increase of the surface acidity with decreasing pH of the solution.
- (3) With decreasing pH the W^{4f} signal increases and the La^{3d} signal decreases drastically and vice versa.

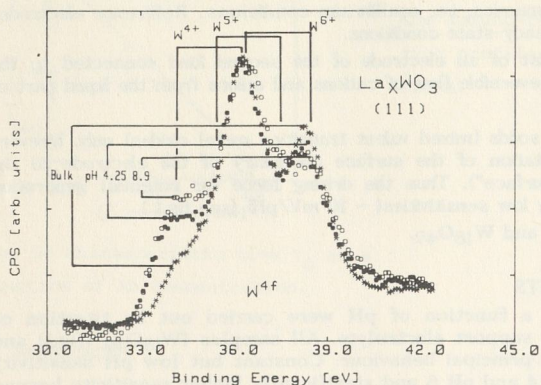


Fig.2
 W^{4f} -spectra of an $La_{0.18}WO_3$ single crystal after conditioning (ca.12h) in solutions of different pH.

These results prompt the idea of a "Chameleon Surface" which adapts its surface acidity ($W^{+6}/W^{+5}/W^{+4}$ -proportions) to the acidity (pH) of the solution as a result of steady state corrosion processes. Consequently the driving force of the potential generating process at the solid/liquid interface is decreased in accordance with the observed sub-Nernst sensitivity.