

Chubb, T.A. *Production of excited surface states by reactant starved electrolysis.* in *The 9th International Conference on Cold Fusion, Condensed Matter Nuclear Science.* 2002. Tsinghua Univ., Beijing, China: Tsinghua Univ. Press.

PRODUCTION OF EXCITED SURFACE STATES BY REACTANT STARVED ELECTROLYSIS

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ABSTRACT

Starved reactant electrolysis can result in co-deposition of hydrogen and a higher voltage reactant. The hydrogen has the potential to be deposited in an excited state that is delocalized and wavelike. It is suggested that this occurred in the Liaw et al. study. Evidence for cathodic overpotential electrolysis in molten hydroxide electrolyte is presented.

1. INTRODUCTION

Addressing the Coulomb barrier problem Schwinger stated, "In the very low energy cold fusion, one deals essentially with a single state, described by a single-wave function, all parts of which are coherent. A separation into two independent, incoherent factors is not possible, and all considerations based on such a factorization are not relevant."^[1] Summarizing their hydrogen-metal experimental studies, Chernov et al. state, "The experimental results testify: -H atoms occupy regular positions in the crystal lattice, form their own H subsystem – In this subsystem H atoms are connected with each other a much stronger than with atoms of the matrix."^[2] Astaldi et al., referring to H atoms adsorbed on Cu, state that "in the low coverage limit, H atom motion is conveniently described in terms of 'protonic' energy bands (fully delocalized H atoms)."^[3] Wavelike H atoms covering a sufficiently large crystal can overlap each other and are merged by exchange. Exchange results in a closer H-H coupling than the coupling of single H atoms to the lattice. Chubb and Chubb have shown that an exchange-symmetrized, many-body wave function, which is a single-wave function, can undergo radiationless cold fusion.^[4] Puska and Nieminen have calculated energy levels for wavelike quantum-delocalized H on Ni (111), as shown in Fig.1.^[5] Fig. 1 shows that the excited states of adatom H are delocalized band states with periodic symmetry. The bottoms of the energy bands are of the order of 0.1eV above the ground state.

This work seeks to develop improved means for electrolytically depositing D atoms onto a metal surface into an excited state, so as to populate a delocalized ion band state. It builds on the cold fusion study by the Liaw et al., which used molten salt electrolysis.^[6] Unfortunately, their work has not been successfully repeated. The Liaw et al. study showed large

amounts of excess heat in a D-Pd system at elevated temperature under overvoltage conditions, as shown in Figs 2 and 3. Liaw et al. anodically deposited D⁻ ions onto a Pd ingot anode. The chemistry was unusual in that during heat production the electrolysis seemed to have occurred under D⁻ ion-starved conditions.

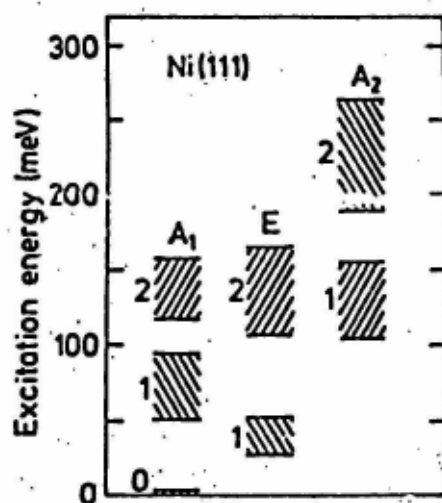


Figure 1. Energy Level structure for H adsorbed on Ni(111) for Ref.3

Interestingly, during this electrolysis, a shuttle mechanism seemed to have occurred, which recycled deuterium between anode and cathode. This shuttle was described by Liaw and Liebert.^[7] It is basically equivalent to a co-deposition of D^- and Cl^- ions so as to produce DCl at the anode, followed by reaction of DCl with Li metal that had been deposited on the cathode. The resulting $LiCl$ and LiD dissolves into the molten salt, replacing the D^- and Cl^- ions consumed. The overvoltage for deuterium deposition on the anode was of the order of 1.7 volts, assuming Li metal deposition on the cathode. This energy and the deposited D atoms presumably created and maintained a collection of delocalized many-body deuterium subsystems. Radiationless cold fusion reactions are expected to occur within the individual deuterium subsystems, generating the observed excess heat.

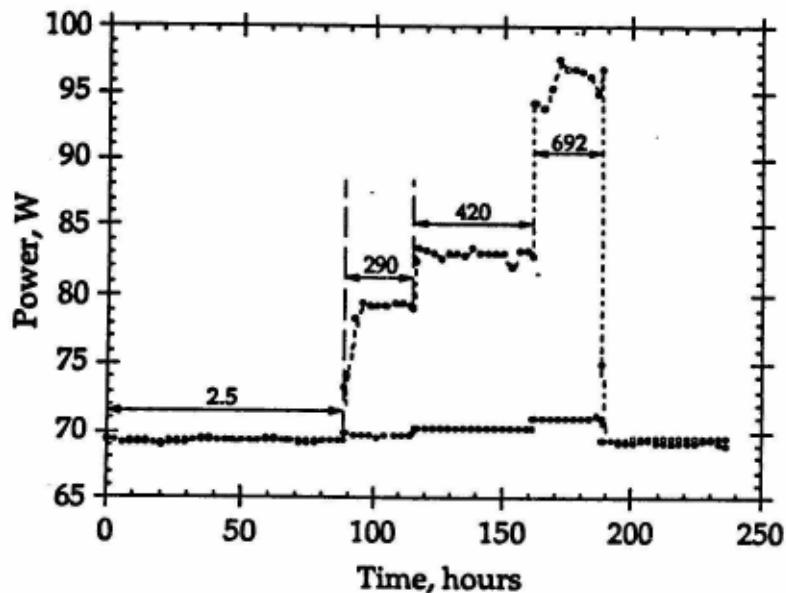


Figure 2. Total heat power out and oven + electrolysis power in vs. run time by Liaw et al.

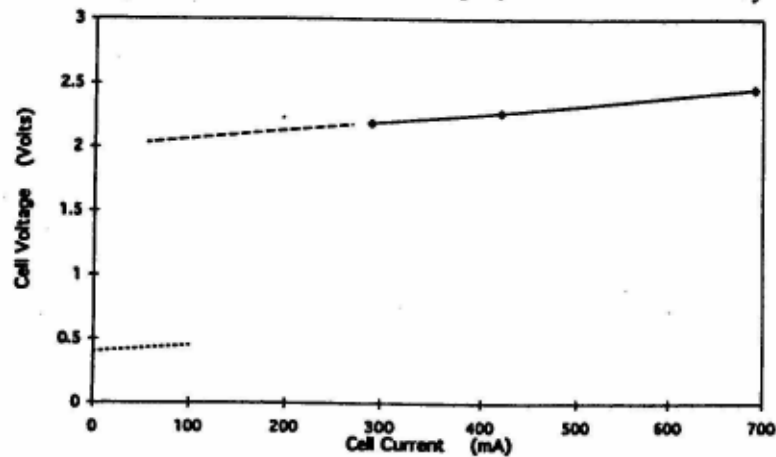


Figure 3. Cell voltage vs. cell current during Liaw et al. heat producing run

I describe an exploratory study of molten hydroxide electrolysis. Current work uses molten $NaOH$, KOH at the 1:1 molar eutectic composition. The eutectic melts at $170^{\circ}C$. Current studies are carried out at $\sim 200^{\circ}C$ in a Teflon beaker under flowing Argon. Chemistry in the eutectic is described by Plambeck's paper in Bard's "Encyclopedia of Electrochemistry of the Elements".^[8] The hydroxide chemistry is an analog of solution chemistry in water. It replaces the pH characterization of water solution chemistry with a pH_2O characterization of solutions in the hydroxide. The pH_2O is defined as the negative Log of the molar concentration of H_2O . Molar concentration $[H_2O]$ is maintained by the reaction $2OH \leftrightarrow H_2O + O^-$. For $pH_2O < 5.75$, the solution is called "acid", and for $pH_2O > 5.75$, the solution is called "basic". When the system

is acid, the reaction $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^- + \text{H}_{\text{ads}}$ deposits H atoms on the cathode. Under starved H_2O conditions, i.e. at higher pH₂O, cathode electrons are shared between the above reaction and the reaction $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}_{\text{metal}}$. Co-deposition of H and Na occur, and the H is deposited on the cathode at an overpotential. It is unknown whether a cathodic overpotential of this type using an oxydeuteride melt would support formation of a D⁺ ion band state subsystem, as seems to have occurred in the Liaw et al. study.

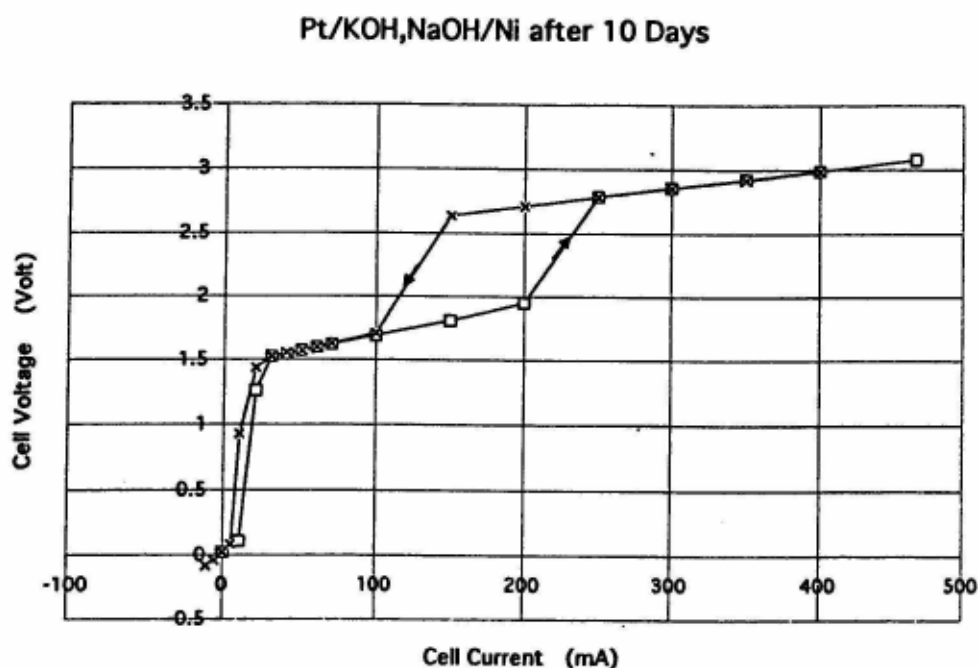


Figure 4 Voltage vs. Current during starved electrolysis with Ni cathode: Pt/KOH,NaOH/Ni.

Fig. 4 shows a voltage vs. current curve measured during starved water electrolysis with a Ni cathode and Pt anode. The electrolyte had been dried by 10 days of electrolysis at 0.4 A. The squares show voltages recorded during a stepwise increase in cell current. The individual readings are taken at 2-minute intervals. The x's are readings taken during a similar stepwise decrease in cell current. The discontinuity in voltage is believed to be caused by the increased voltage required to co-deposit Na along with hydrogen. The hysteresis is believed a result of localized water depletion near the cathode. There is more water following a period of low current and less water following a period of high current. Diffusion does not fully even out reactant concentrations by the end of 2 minutes. The indicated overpotential is about 0.8 Volts. When there is a higher concentration of water in the electrolyte, only the range of voltage corresponding to reduction of water is observed over the indicated current range.

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