Excess of Power During Electrochemical Loading: Materials, Electrochemical Conditions and Techniques

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Signals well above the measurement uncertainties are confirming the anomalous production of excess of power during electrochemical loading of Palladium with Deuterium.

Excess of power has the following features:
1) Threshold effect (loading D/Pd > 0.9)
2) Unobserved with hydrogen
3) Unexplainable as chemical effect
4) Occurs only if materials are showing specific characteristics
Research Approach

1) Material science to increase both reproducibility and signals by loading enhancement.

2) Calorimetric experiments designed to have an appropriate signal/noise ratio.

3) Definition of the effect through the material characteristics.
Calorimetry (Mass Flow): Closed Cells

Closed Electrochemical Cell
NRL Differential Calorimeter

\[ P_{out} = a + b \Delta V \]

\( a = \text{offset} \)
\( b = \text{gain} \)
\( \Delta V = \text{ddp peltier} \)
Some differences were observed concerning Pd cathodes loaded above the threshold $D/Pd = 0.9$:

1) High power gain during the excess.

2) Low power gain during excess.

3) No excess.

The different behavior was related to some features of the samples ascribed to contaminants.
Differences in Two Lots from the Same Producer

Spectrum of Contaminants in the Rough Materials (from the producer).

Both lots 99.95% purity

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I lot: Reproducibility > 60%, Excess Power > 100%

II lot: Reproducibility < 20%, Excess Power < 20%
Effect of Contaminants

Contaminants may act on:

- Grain size
  - Controls Stress and Mass Transfer
- Crystal orientation
  - Controls Kinetics and DL Capacitance
- Grain boundary
  - Controls Stress and Mass Transfer
- Surface treatment → Surface Morphology
  - Acts on Kinetics and DL Capacitance

Lot 1 From the same producer; same treatment  Lot 2
Identified Conditions to Observe the Effect in PdD System

1) Appropriate metallurgy to achieve the loading threshold

2) Enhanced mass transfer

3) <100> mostly oriented material

4) Appropriate surface morphology
Surface

- Crystal orientation and specific contaminants modify the effect of the chemical etching leading a different surface status.

- The surface morphology is acting on the interface electrochemical structure.

Power Spectral Density Function (PSDF) has been selected as surface merit figure.

Two periodicity system
Typical Surface Morphology (after Etching) giving Excess of Heat

PSDF of sample #64 producing 3500% excess of heat.

PSDF of sample L25 producing up to 250% excess of heat.
The larger the PSDF amplitude the larger the excess of power.

PSDF of sample ET-UTS-05 producing 25% excess of heat under electrolysis.

PSDF of a sample not producing excess of heat.

Surface morphology results to be a fourth condition.
Now we play with contaminants
The experimental evidences allowed to produce a material with characteristics close to the ones above described.

A lot of Pd having a spectrum of contaminants approaching the lot 1 was undergone to the treatment leading to: dominant <100> orientation and an appropriate metallurgy.

L66 ESBD Results
Palladium was doped by Platinum: effect on the surface

L66 (120-160) Platinum added

up to 25-30% excess
Again

L66 (160-200) Platinum added

up to 25-30% excess
Palladium Rhodium Alloy produced at ENEA by using NRL protocol

L119 (20-60) Before

L119 (20-60) PSD from AFM
EBSD reveals a scattered orientation of crystals and small size grains

Loading is high and fast
L119 Palladium Rhodium Alloy produced at ENEA by using NRL protocol

We control the excess of power, 50 times larger than a chemical effect.
Cu, Fe, Si and Pt have been identified as contaminants on the electrode surface after the electrolysis.
Let see if we may extract any additional information from GEIS (Galvanostatic Electrochemical Impedance Spectroscopy) performed during the experiment.
Typical GEIS Performed with Inactive Pd Foil

GEIS at two DC current levels

4 KHz

30 mA + 3* sin(ωt)

100 mA + 10* sin(ωt)

2 Hz
In Situ Electrochemical Impedance Spectroscopy on Sample L119(20-60) Excess-off

Excess-Off

Eis 30mA/3mA 15 kHz – 5Hz

Excess-Off

Depression angle
φ=(1-n)*90  D=1+1/n
D Fractal dimension

Excess-Off

Eis 30/3  400 kHz- 5 Hz
Current and overvoltage behavior during 40% excess

Note: Current ripple has been always observed in galvanostatic mode during significant excesses
Something was changing at the interface during the excess!!

$\phi = -26^\circ$

$D = 2.4$
In Situ Electrochemical Impedence Spectroscopy on Sample L119(20-60) Excess-on

A wide range of resonating frequencies is possible
Calorimeter check: Pin-Pout by applying 100mA ± 20mA in the frequency range 1MHz-1Hz
Sample L119-140-180

Sample L119-140-180 was inactive, no evidence of specific contaminants on the surface.
Again

L124(50-90) Excess

Pin – Pout L124(50-90)

Normalized resistance L124(50-90)

Loading is high and fast

Identified contaminants: same as L119(20-60)

This sample was the ‘most close’ to L119(20-60)
Conclusions

Material features, related with the occurrence of the effect, have been identified: 1) loading threshold, 2) loading dynamics, 3) grain-grain boundary size, 4) surface morphology, 5) crystal orientation (Pd).

A specific role of some contaminants has been also identified.

In situ GEIS revealed a dramatic changing of the electric structure of the interface: resonating circuits components turn out during excess.

Material status is the key to observe the effect. Material science is the key to understand it, since some material characteristics support some processes rather than others.

By applying the scientific method future work should be oriented towards the definition of the effect rather than its demonstration.
Thank You

This work has been supported by National Instruments and a specific work is in progress to develop new instruments to improve the study.