Time-resolved measurement of ruthenium dissolution in direct methanol fuel cells

TECHNISCHE UNIVERSITÄT DARMSTADT

Erneuerbare Energien

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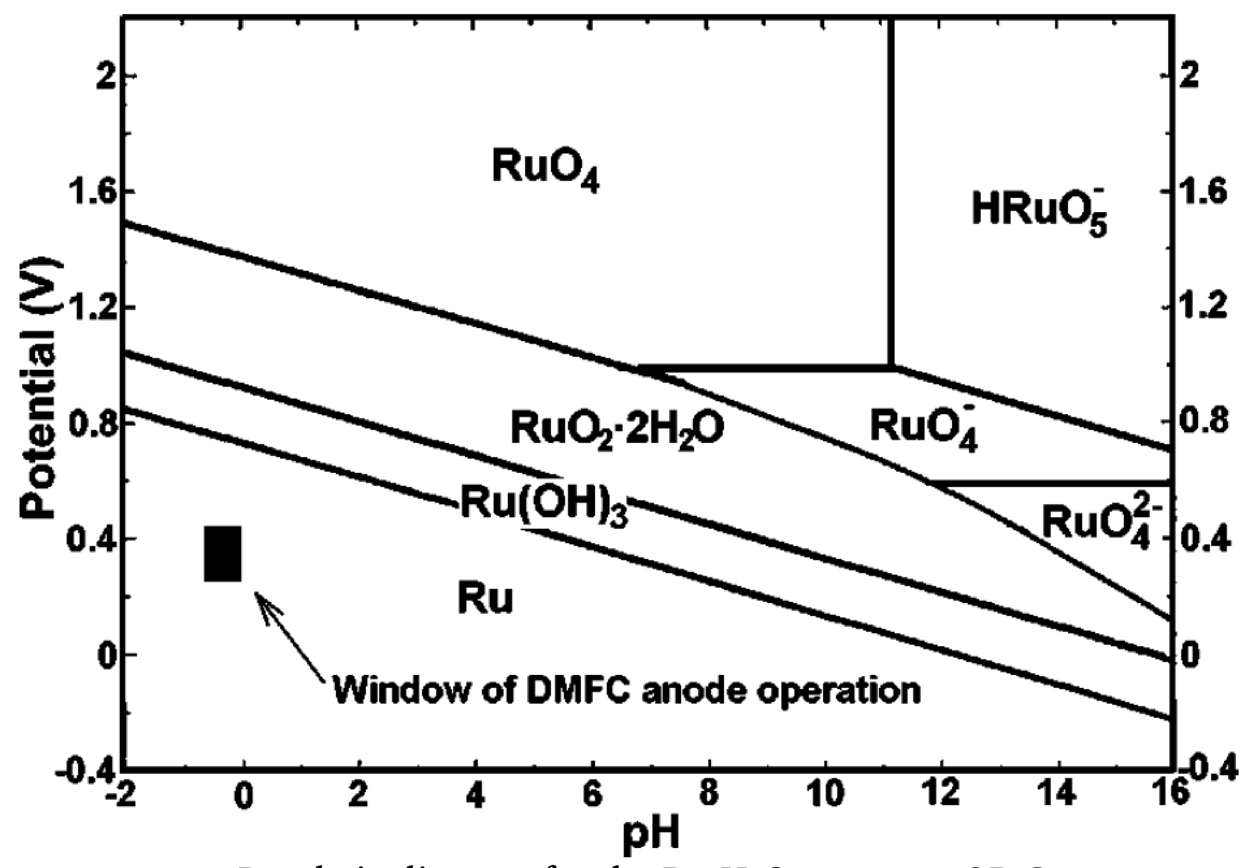
Typical pallet truck

An economic analysis carried out by the Forschungszentrum Jülich together with several industrial partners showed that pallet trucks equipped with DMFC stacks are competitive to battery driven trucks. Due to applications like this, DMFC systems can enter the market and gain the acceptance needed for further market development.

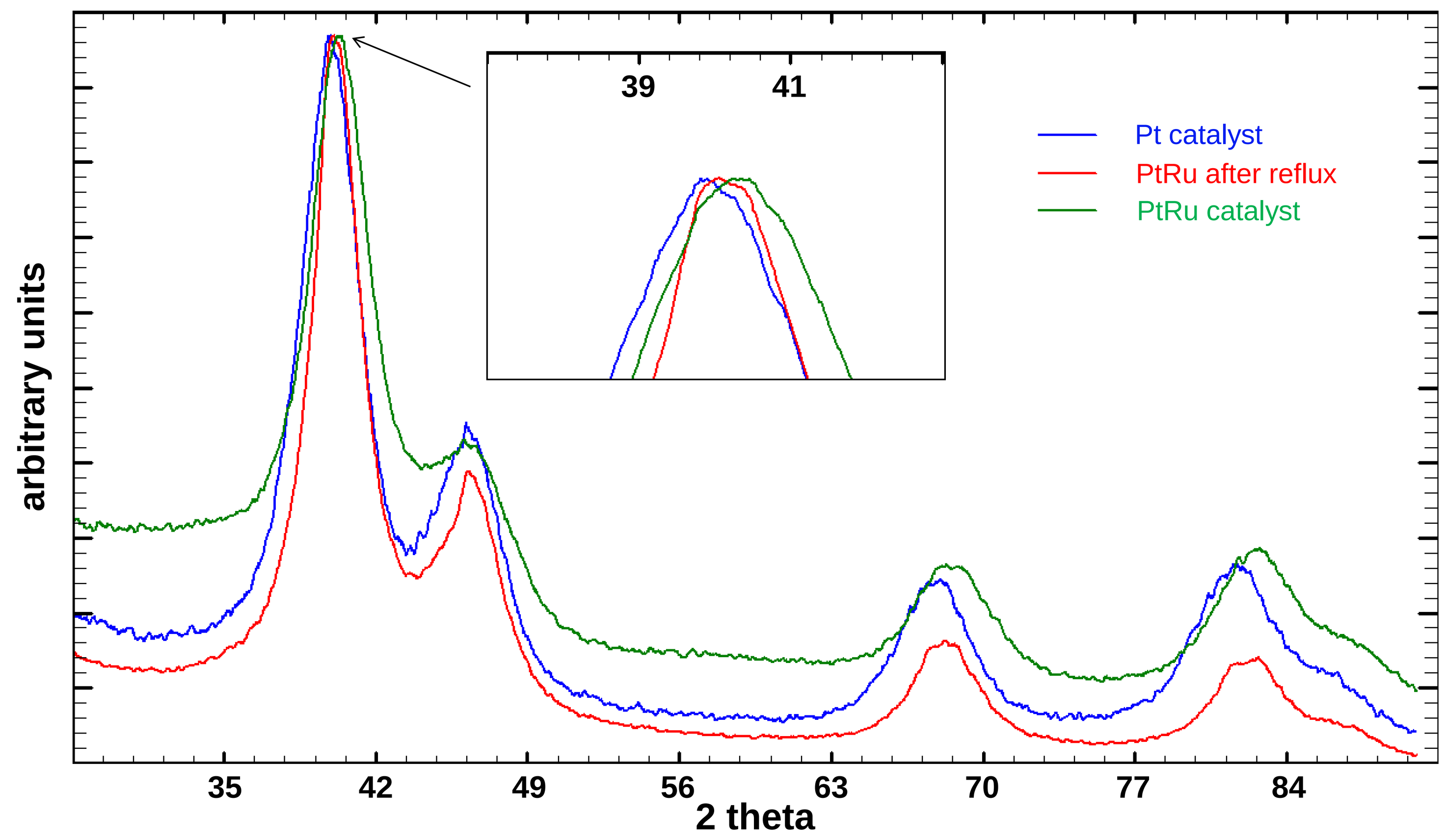
In DMFCs, ruthenium is added to the platinum catalyst on the anode side to provide oxygen-containing species to oxidise CO adsorbates blocking the platinum catalytic surface.

Looking at the phase diagram of Pt-Ru and the Pourbaix diagram of Ru-H_2O, one would assume that Ru is quite stable under fuel cell conditions.

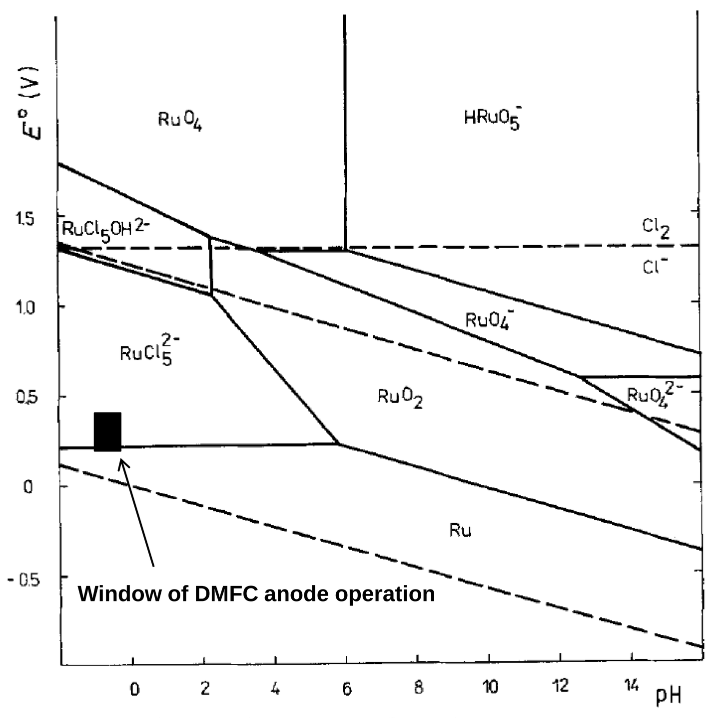


Pourbaix diagram for the Ru-H_2O system at 25 C

However, XRD and EXAFS data of Pt-Ru catalysts show a significant structural change after operation. These changes can be attributed to de-alloying of Pt-Ru and/or Ru dissolution.



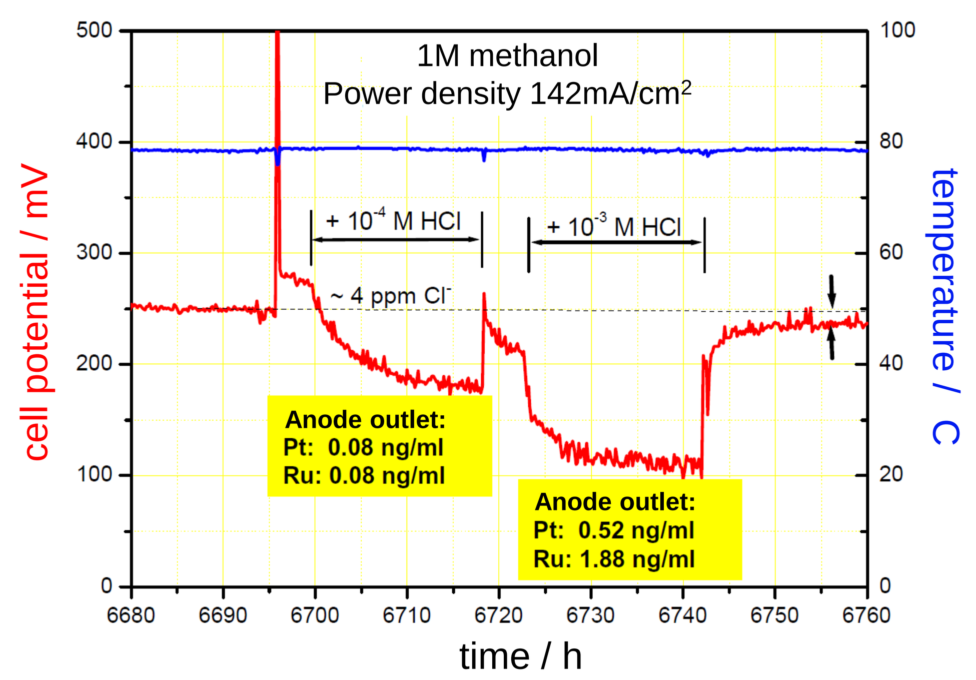
X-ray diffractogram showing the de-alloying of a Pt-Ru catalyst



Pourbaix diagram for the Ru-H_2O-Cl^- system at 25 C

A second Pourbaix diagram, which also considers Cl^- ions, shows Ru dissolution. These impurities could enter the cell with the used fuel.

Experiments using a FC stack and deliberately elevated Cl^- ion concentrations provided evidence for Ru dissolution via ICP-OES analysis of the excess liquid. They also showed that the Ru dissolution leads to cell degradation and power loss.



Ru dissolution test of a FC stack with Cl^- enriched fuel

Consequently this lead to a series of laboratory experiments to mimic the conditions for Ru dissolution in accelerated aging tests:

1. heating catalyst (PtRu on carbon black) mixed with 5% Nafion® solution in 1M methanol under reflux
2. heating catalyst in 1M methanol under reflux
3. heating catalyst in 4M methanol under reflux
4. heating catalyst in 4M methanol and H_2SO_4 (pH ~3) under reflux

For each treatment samples of the solution were taken, centrifuged at 6,000rpm (sample 1) or filtered through a 0.1micron filter (samples 2-4) and analysed by ICP-OES. Obviously there was no electrical potential applied in these experiments. Only the first sample showed a significant amount of Ru in the analysis of the sample solution. This could be due to Ru dissolution in the presence of Nafion®, but further experiments are needed for confirmation.

References:
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T. Loucka, 'The potential-pH diagram for the Ru-H_2O-Cl^- system at 25 C', Journal of Applied Electrochemistry, 20 (1990)
P. Piela et al.,Ruthenium Crossover in Direct Methanol Fuel Cell with Pt-Ru Black Anode', Journal of Electrochemical Society, 151 (2004)