Institute of
Technical Thermodynamics

Modeling of Platinum Particle Growth Mechanisms in Direct Methanol Fuel Cells

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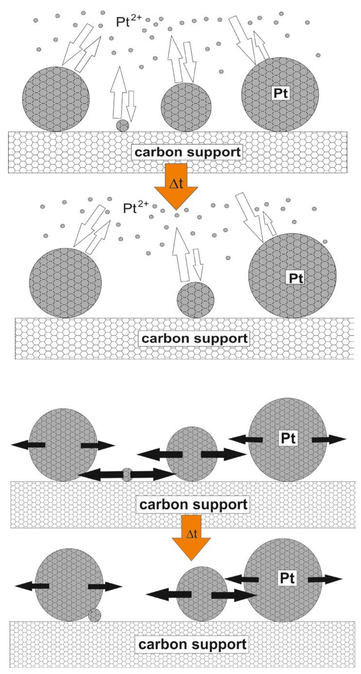
Motivation

- The decrease of the electrochemically active surface area (ECSA) at the cathode side is crucial for the loss of DMFC performance
- The loss of ECSA is related to a growth of the platinum particles
- A better understanding of the underlying mechanisms is important to reduce degradation
- **Goal: development of a physical degradation model for the DMFC cathode catalyst layer**

Modeling Approach



Physical model:

- Particle growth is described by means of a change in the particle size distribution (PSD)
- Mechanisms leading to particle growth:
  - Ostwald ripening (dissolution and precipitation of Pt^{2+})
  - Coalescence due to diffusion of Pt particles
- PtO formation affects Pt dissolution[1]

Mathematical model:

- Balance equation for the particle size distribution:

$$\frac{\partial N(r,t)}{\partial t}+\frac{\partial}{\partial r}\left(N(r,t)\left.\frac{\partial r}{\partial t}\right|_{Ostwald}\right)=\left.\frac{\delta N(r,t)}{\delta t}\right|_{Coal}$$

- Ostwald ripening[2]:

$$\left.\frac{\partial r}{\partial t}\right|_{Ostwald}=k_0\Omega\exp\left(-\frac{E_{act}}{RT}\right)\frac{s_{act}(r)}{s(r)}\left[\exp\left(\alpha\frac{nF}{RT}\Delta\phi\right)\exp\left(\alpha\frac{2\Omega\gamma}{RT}\frac{1}{r}\right)-\nu\frac{c_{Pt^{2+}}}{c_{Pt^{2+}_{ref}}}\exp\left(-(1-\alpha)\frac{nF}{RT}\Delta\phi\right)\exp\left(-(1-\alpha)\frac{2\Omega\gamma}{RT}\frac{1}{r}\right)\right]$$

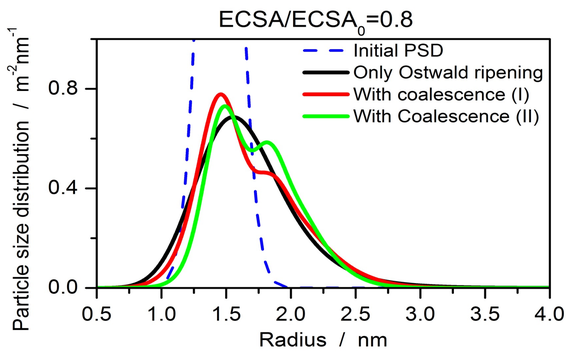
- Coalescence[3]:

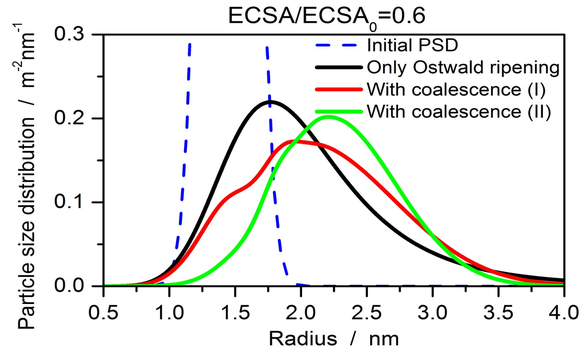
$$\left.\frac{\delta N(r,t)}{\delta t}\right|_{Coal}=r^2\int_0^r D(r')N(r',t)\frac{N((r^3-r'^3)^{1/3},t)}{(r^3-r'^3)^{2/3}}dr'-\int_0^\infty (D(r)+D(r'))N(r,t)N(r',t)dr$$

Mechanisms:
(I) Ion attachment/detachment[4]: $D(r)\sim r^{-1}$
(II) Adatom diffusion[5]: $D(r)\sim r^{-4}$

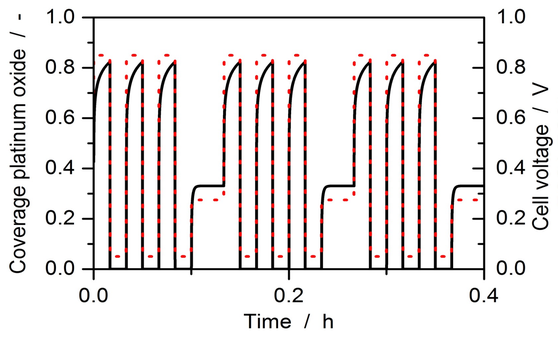
Results

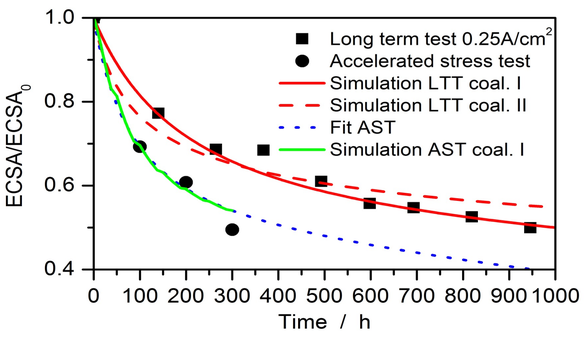
- Evolution of the particle size distribution strongly depends on the mechanisms



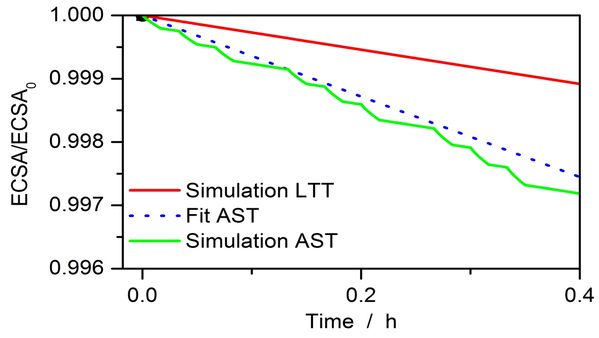


- The model has been validated with aging tests of Casalegno et al.[6]
  - Long term test (LTT) at 0.25A/cm²
  - Accelerated stress test (AST): High cathode potential due to periodic air interruption





- Coalescence model (I) is in good agreement with the experimental time evolution of the ECSA
- Periodic air interruption leads to lower PtO coverage and accelerated degradation



Summary and Outlook

A detailed platinum particle growth model has been developed to describe the degradation of the DMFC cathode catalyst layer. It has been included into a DMFC cell model and validated on a first set of degradation experiments.

Future work:
Investigations on reversible degradation mechanisms and coupling effects between reversible and irreversible degradation.

References

[1]: E.F. Holby, W. Sheng, Y. Shao-Horn and D. Morgan, *Energy & Environmental Science* 2 (2009) 865
[2]: E.F. Holby and D. Morgan, *Journal of the Electrochemical Society 159* (2012) B578
[3]: E. Ruckenstein and B. Pulvermacher, *Journal of Catalysis* 29 (1973) 224
[4]: S.V. Khare, N.C. Bartelt, T.L. Einstein, *Physical Review Letters* 75 (1995) 2148
[5]: F. Behafarid, B.R. Cuenya, *Surface Science* 606 (2012) 908
[6]: A. Casalegno et al. (Politecnico di Milano), *Premium Act final report* (2014)

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