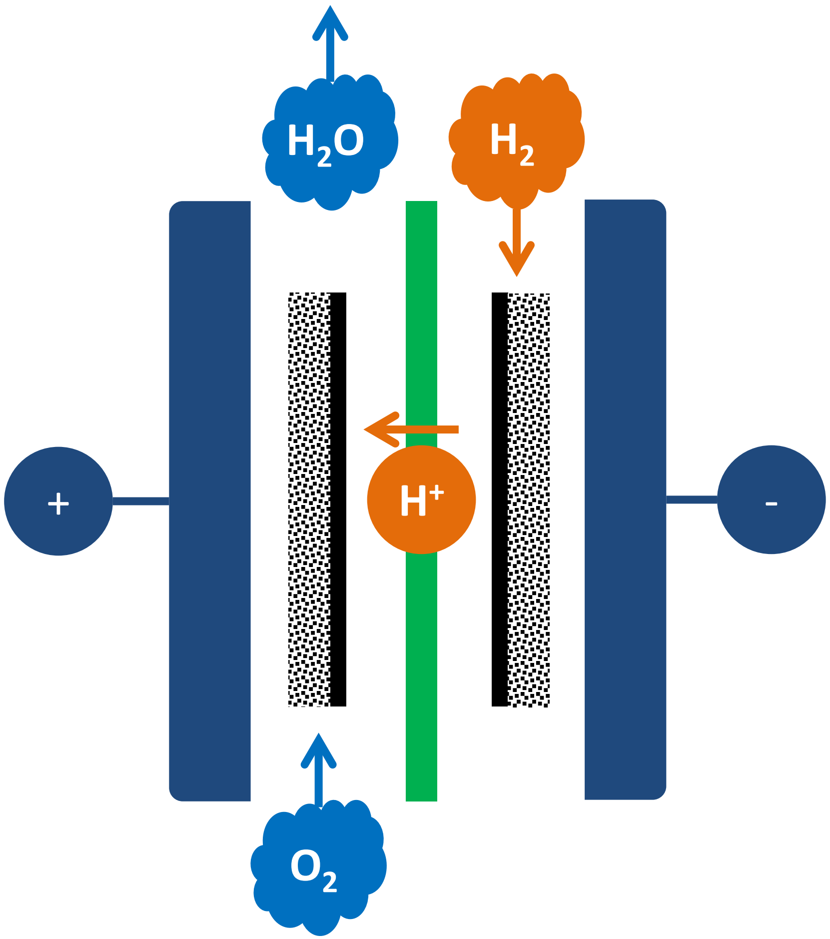
Kinetics of H_3PO_3 oxidation on a bulk Pt electrode

UCT PRAGUE

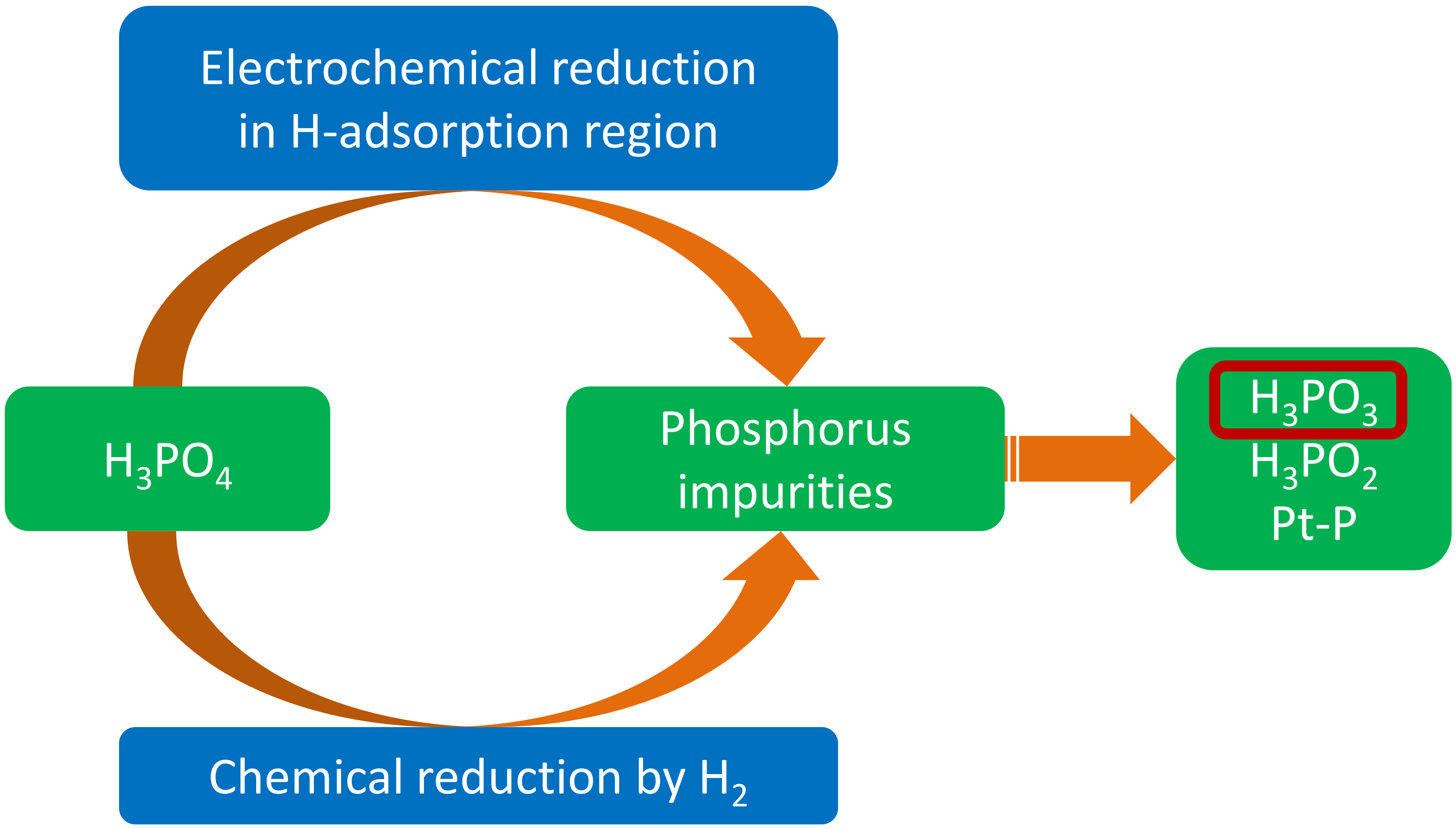
M. Prokop, T. Bystron, K. Bouzek
Department of Inorganic Technology
prokopm@vscht.cz

High-temperature PEM fuel cell



- Operating temperature 120–200 °C
- Polybenzimidazole-type polymer doped with H_3PO_4 as PEM

H_3PO_4 stability on Pt electrode



Motivation and goal

Better understanding of processes during HT PEM FC operation

Prolongation of lifetime

Increase of performance

- Determination of H_3PO_3 electrochemical oxidation kinetics on Pt electrode
- Description of H_3PO_3 oxidation mechanism

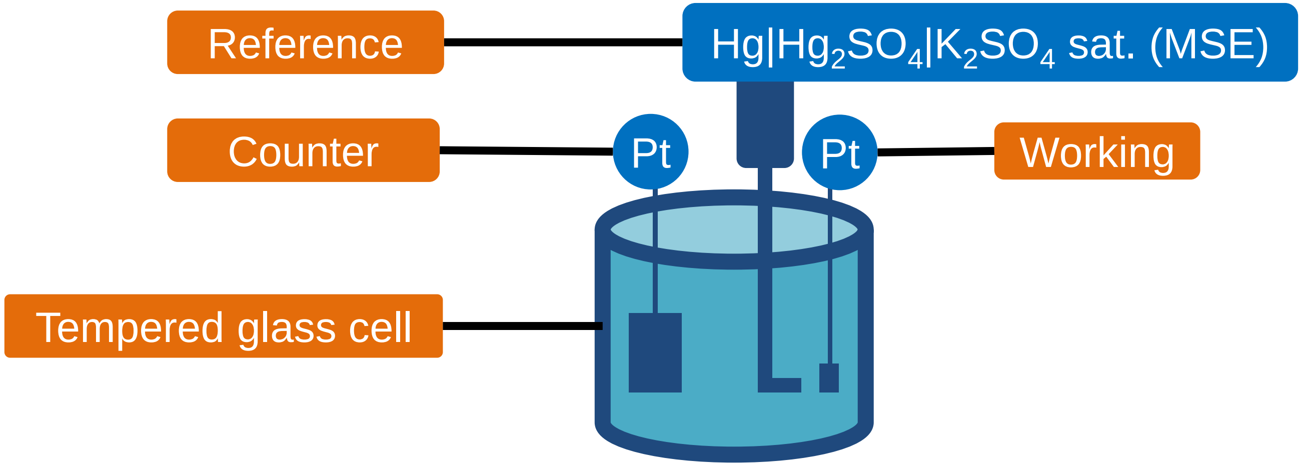
Experimental setup

Instrumentation and methods:

- Potentiostat HEKA PG310
- Cyclic voltammetry v = 50 mV s^{-1}
- Potentiostatic sampling voltammetry

Basic electrolytes:

- 0.5 mol dm^{-3} H_2SO_4
- 0.5 mol dm^{-3} H_3PO_4
- 95% H_3PO_4

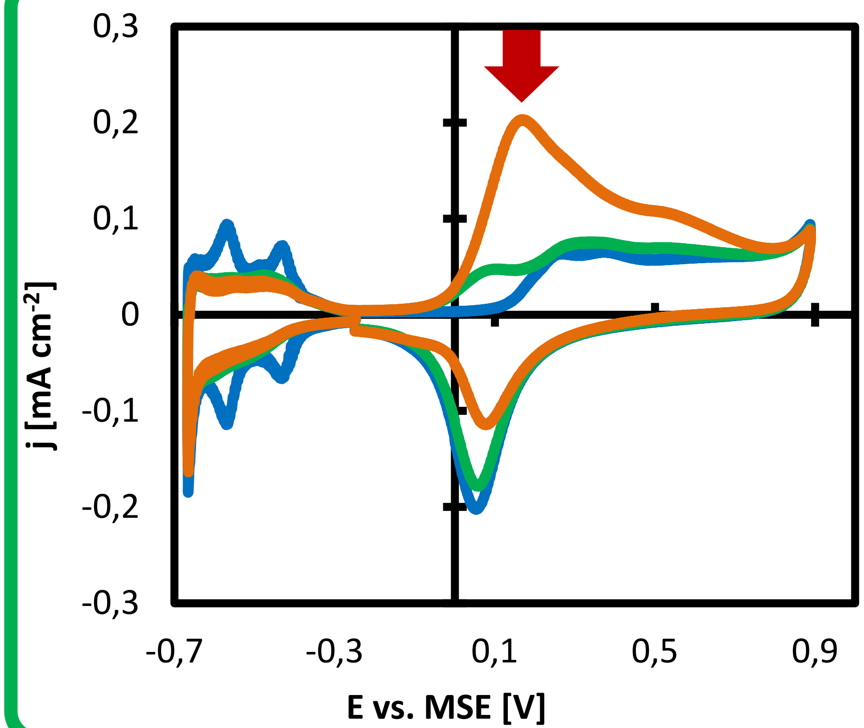


H_3PO_3 electrochemical behavior on Pt

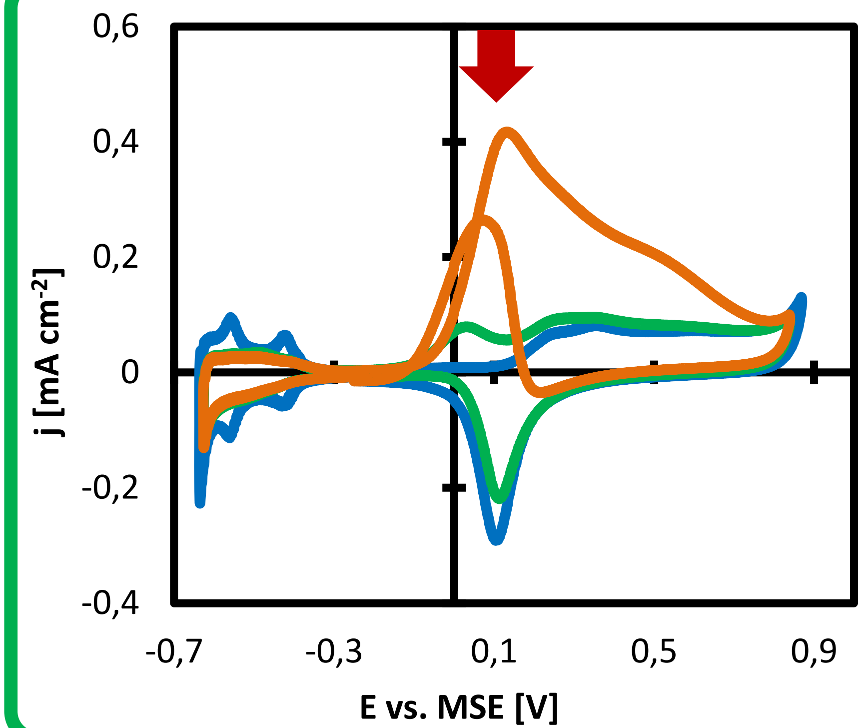
0.5 mol dm^{-3} H_2SO_4

- 0.5 mol dm^{-3} H_2SO_4
- 0.5 mol dm^{-3} H_2SO_4 + 0.1 mmol dm^{-3} H_3PO_3
- 0.5 mol dm^{-3} H_2SO_4 + 1 mmol dm^{-3} H_3PO_3

25 °C



70 °C



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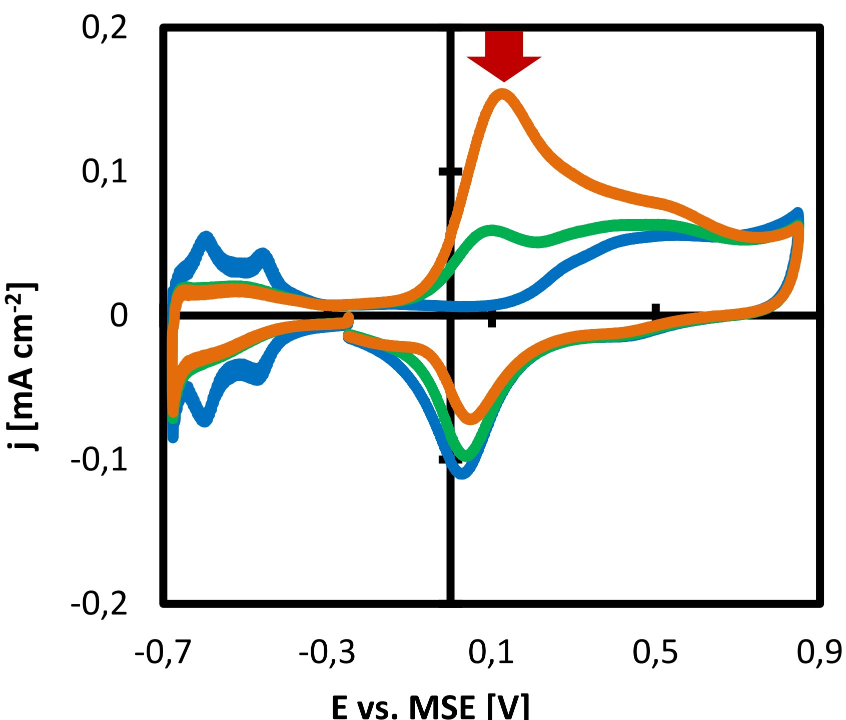
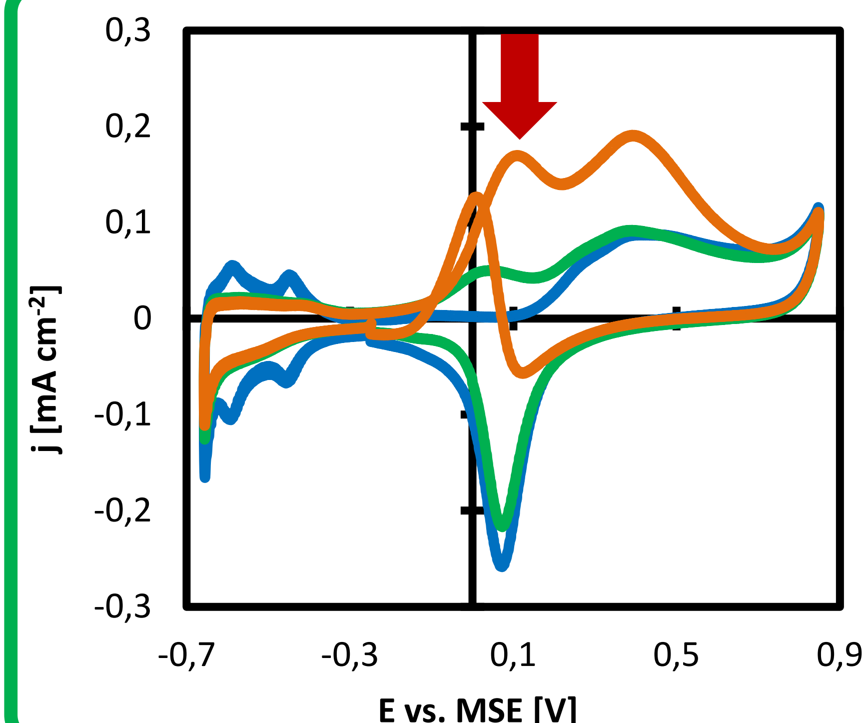


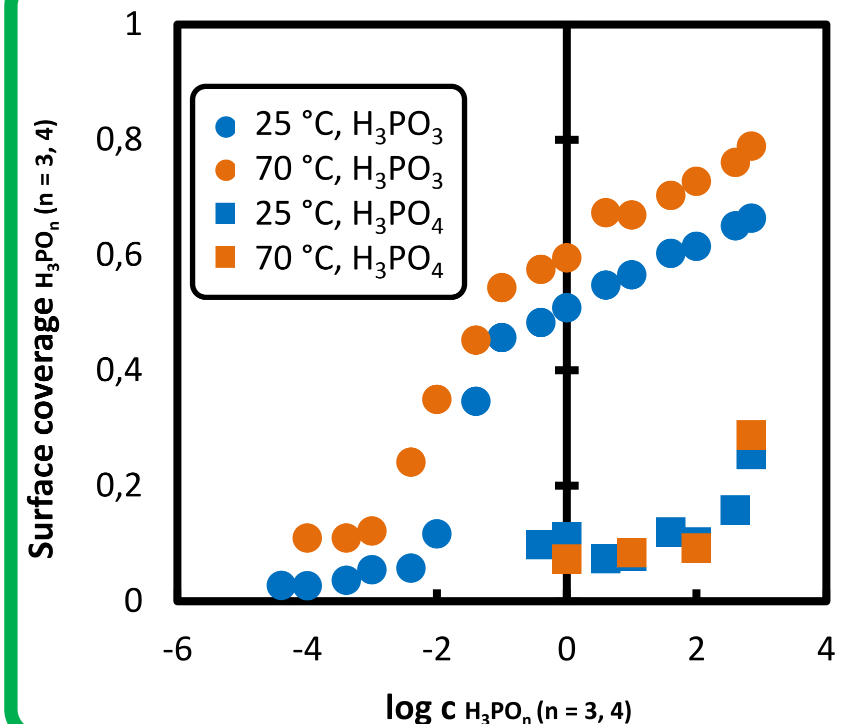
70 °C

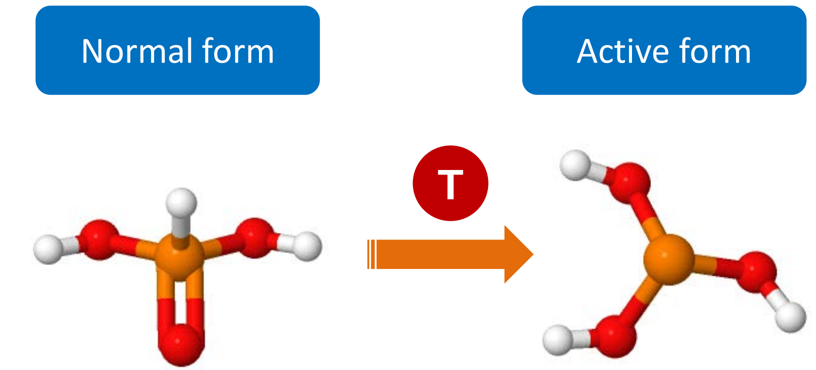


H_3PO_3 and H_3PO_4 adsorption isotherms

Surface coverage by H_3PO_3 increases with temperature

Tautomeric equilibria influenced by temperature

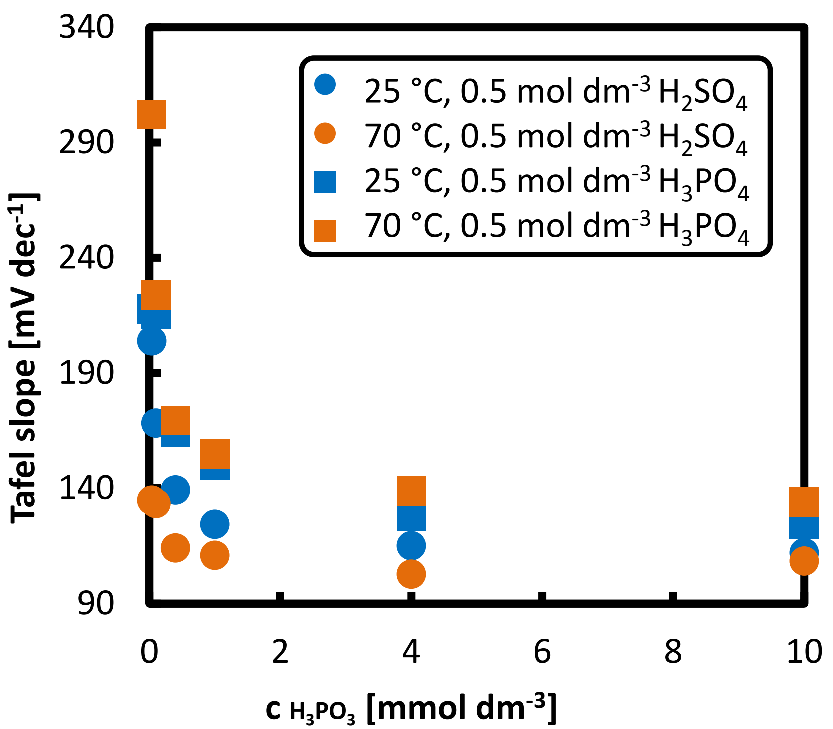


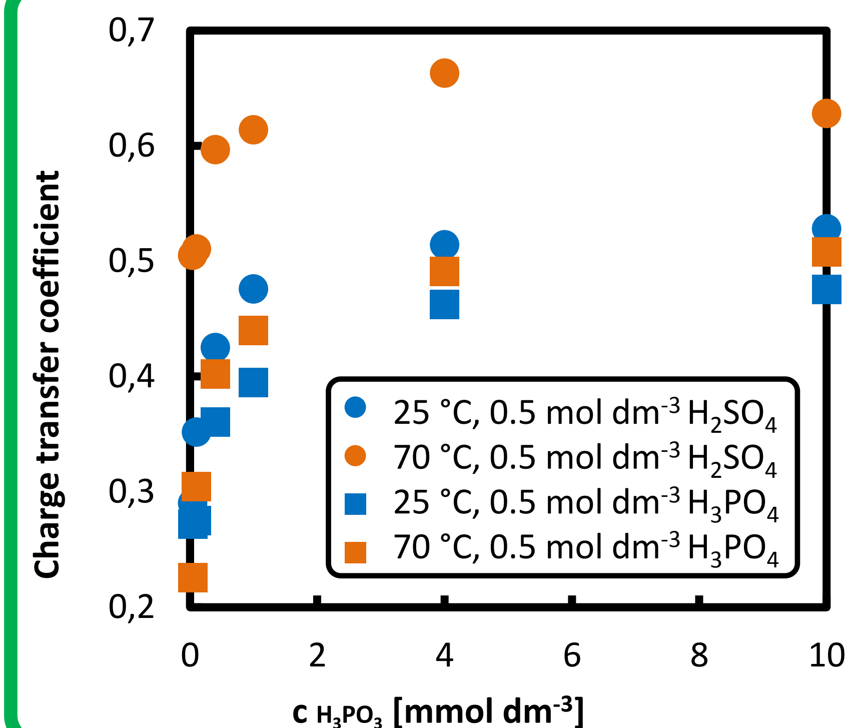


Kinetics of H_3PO_3 oxidation

Tafel slope dependent on H_3PO_3 concentration

At higher concentrations of H_3PO_3 charge transfer coefficient ≈ 0.5

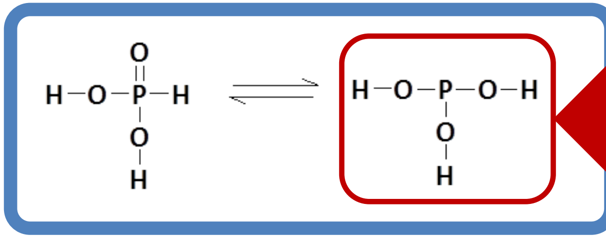




Mechanism of H_3PO_3 oxidation

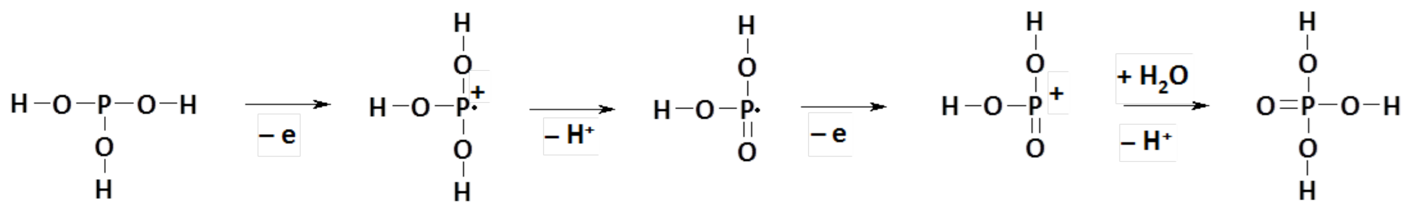
Tautomerization of H_3PO_3 to active form

Adsorption of active form on Pt is initial step

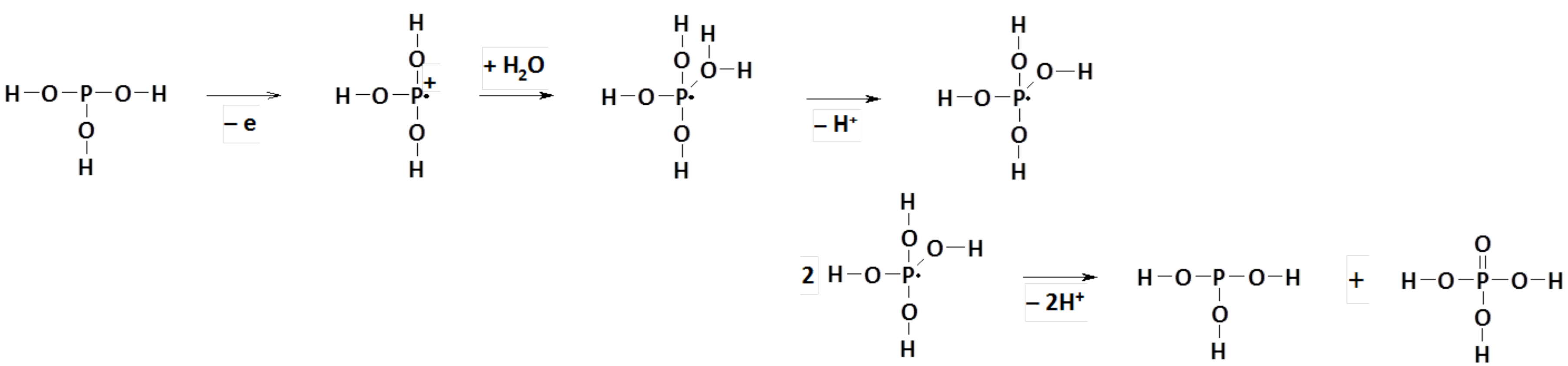


Active form

ECEC oxidation mechanism to H_3PO_4



ECCD oxidation mechanism to H_3PO_4 and H_3PO_3 with P (IV) as intermediate

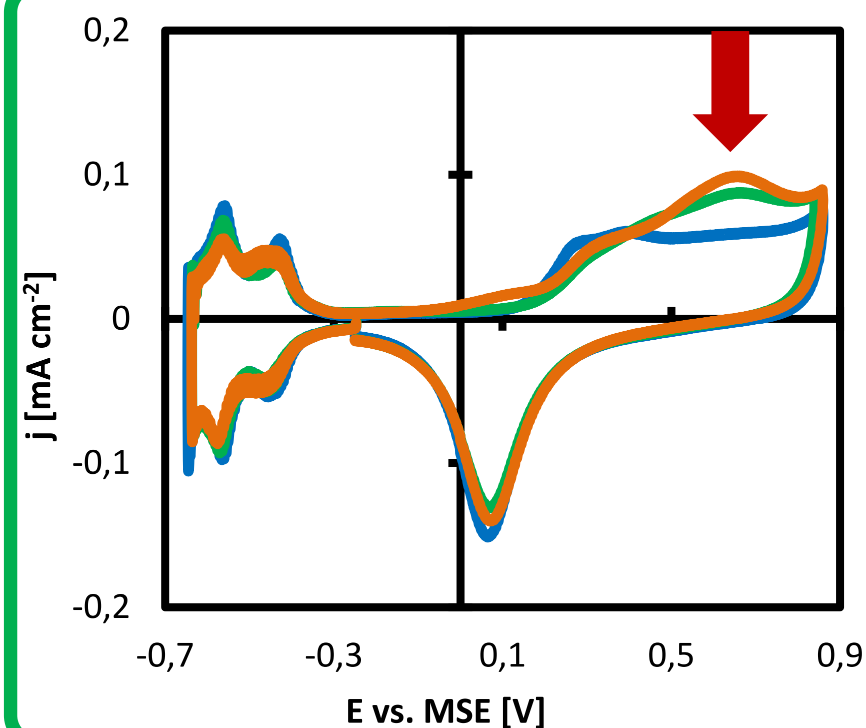


$H_4P_2O_6$ electrochemical behavior on Pt

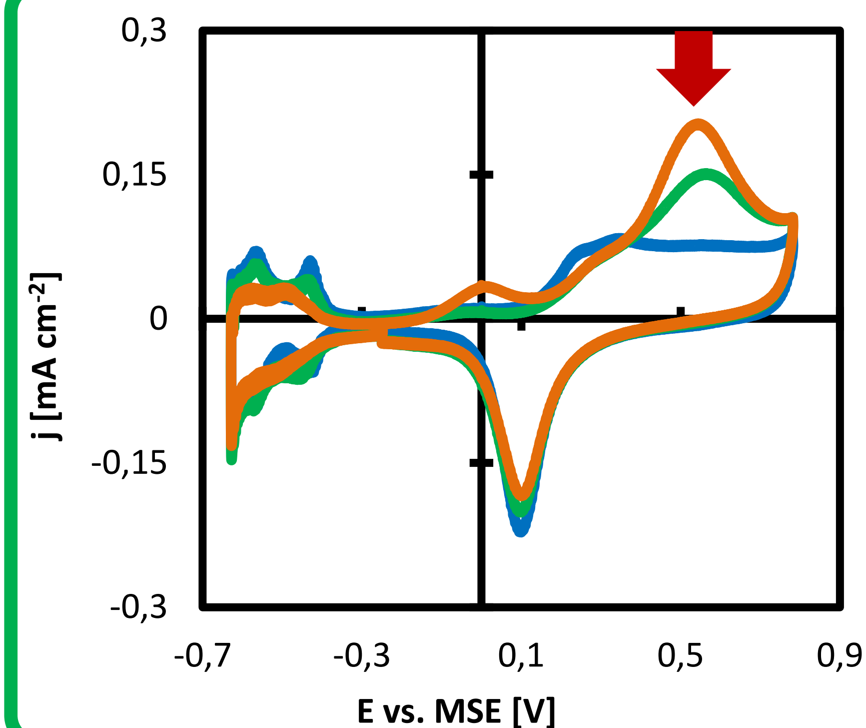
0.5 mol dm^{-3} H_2SO_4

- 0.5 mol dm^{-3} H_2SO_4
- 0.5 mol dm^{-3} H_2SO_4 + 1 mmol dm^{-3} $H_4P_2O_6$
- 0.5 mol dm^{-3} H_2SO_4 + 10 mmol dm^{-3} $H_4P_2O_6$

25 °C



70 °C



$H_4P_2O_6$ electrochemical behavior on Pt

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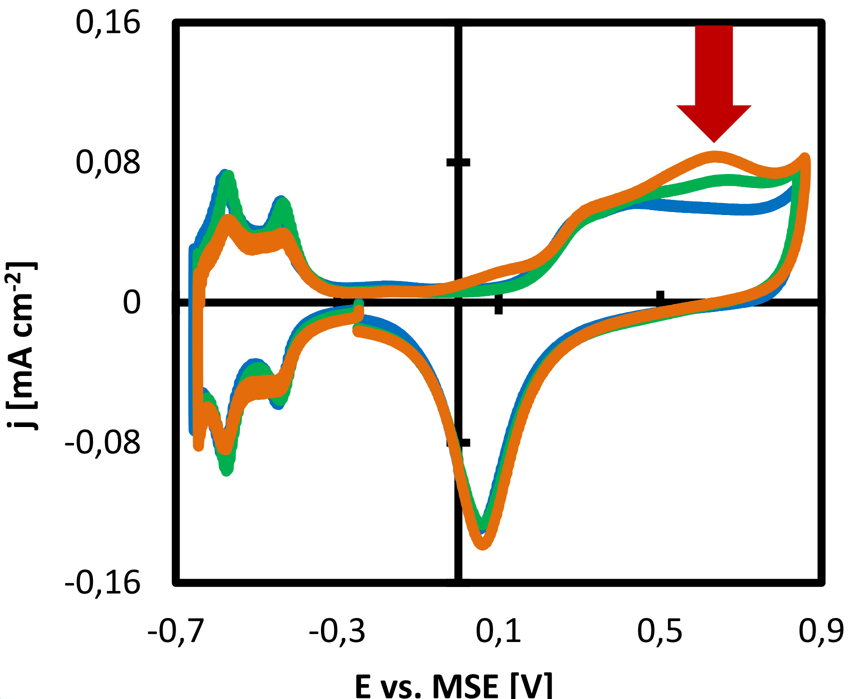
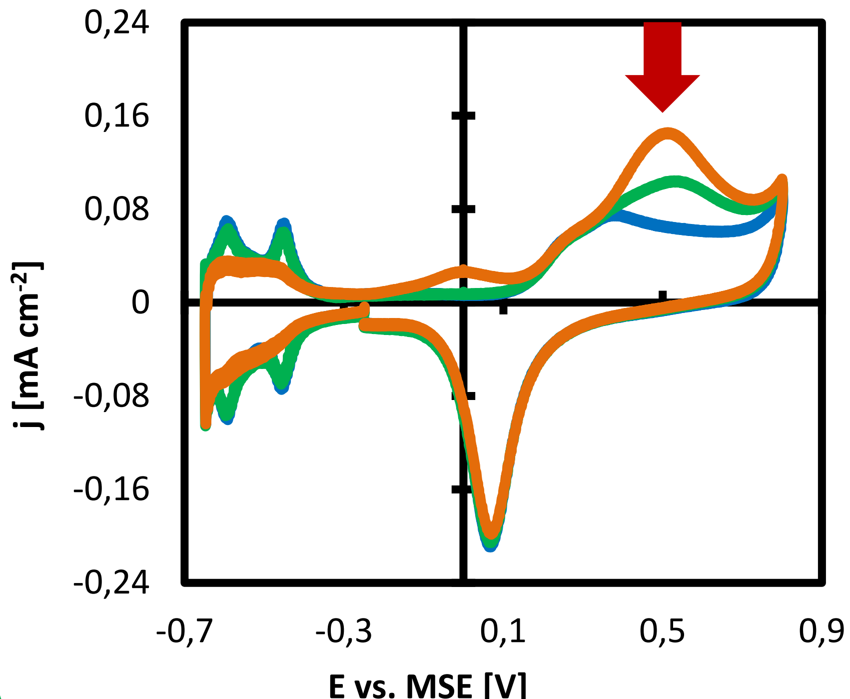


70 °C

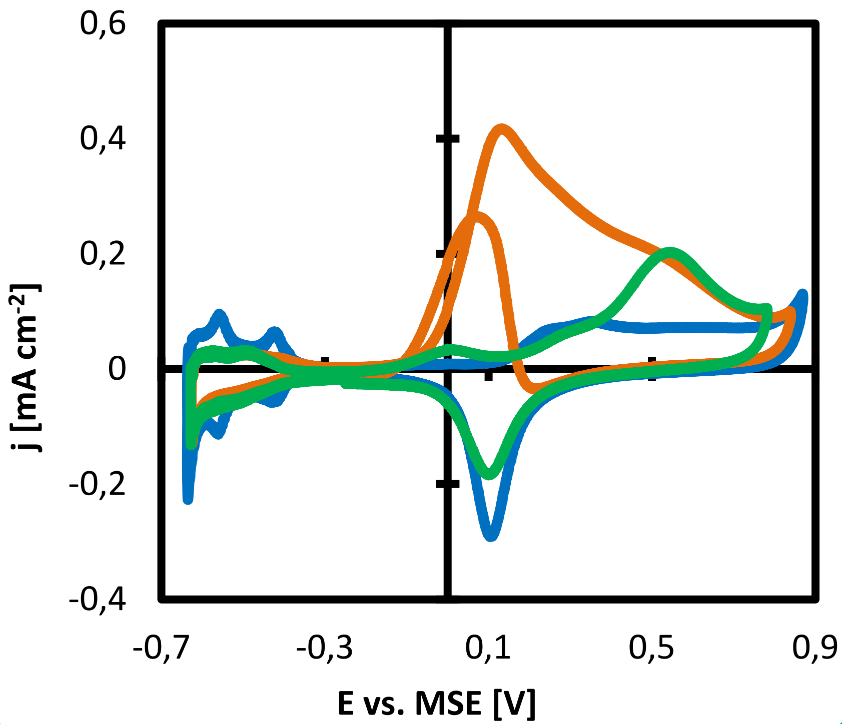


Comparison between H_3PO_3 and $H_4P_2O_6$

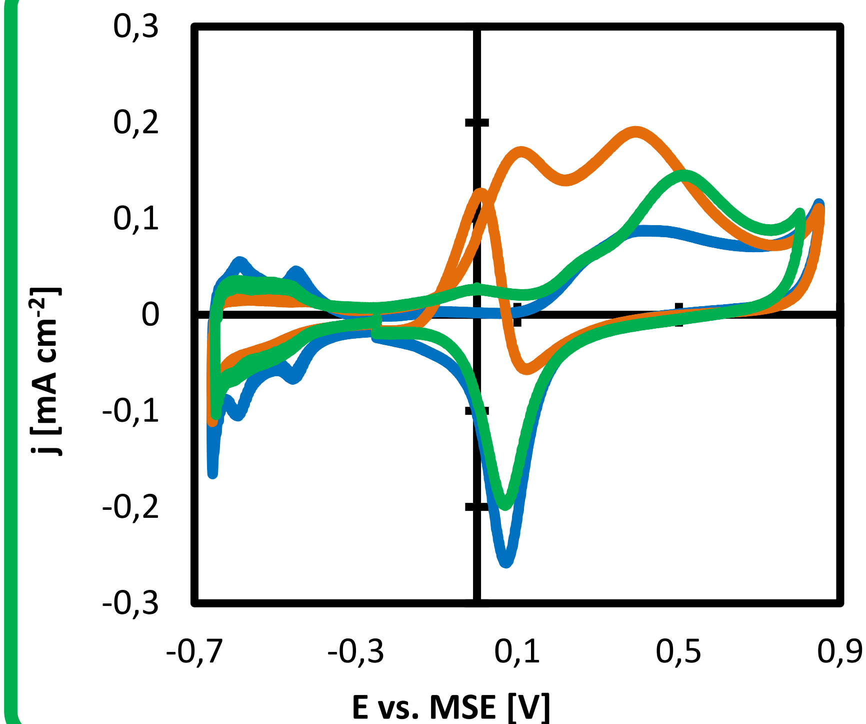
- 0.5 mol dm^{-3} H_2SO_4
- 0.5 mol dm^{-3} H_2SO_4 + 10 mmol dm^{-3} $H_4P_2O_6$
- 0.5 mol dm^{-3} H_2SO_4 + 1 mmol dm^{-3} H_3PO_3

- 0.5 mol dm^{-3} H_3PO_4
- 0.5 mol dm^{-3} H_3PO_4 + 10 mmol dm^{-3} $H_4P_2O_6$
- 0.5 mol dm^{-3} H_3PO_4 + 1 mmol dm^{-3} H_3PO_3

70 °C, 0.5 mol dm^{-3} H_2SO_4

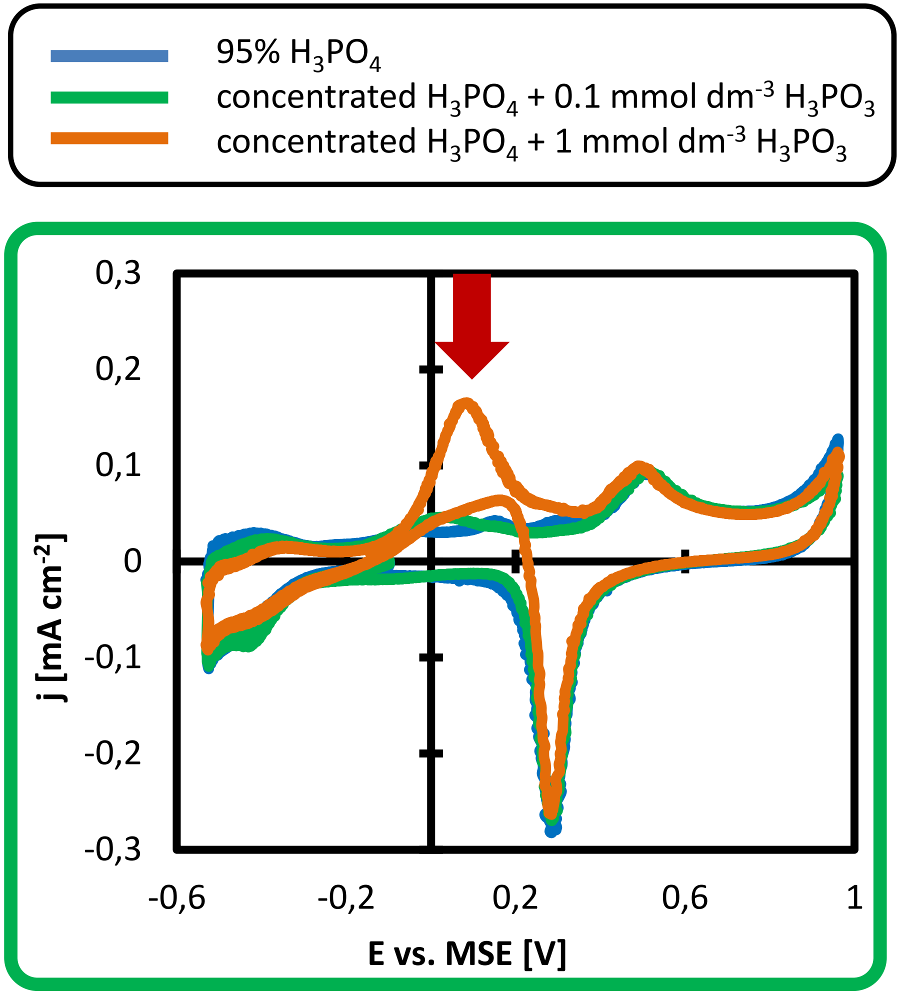


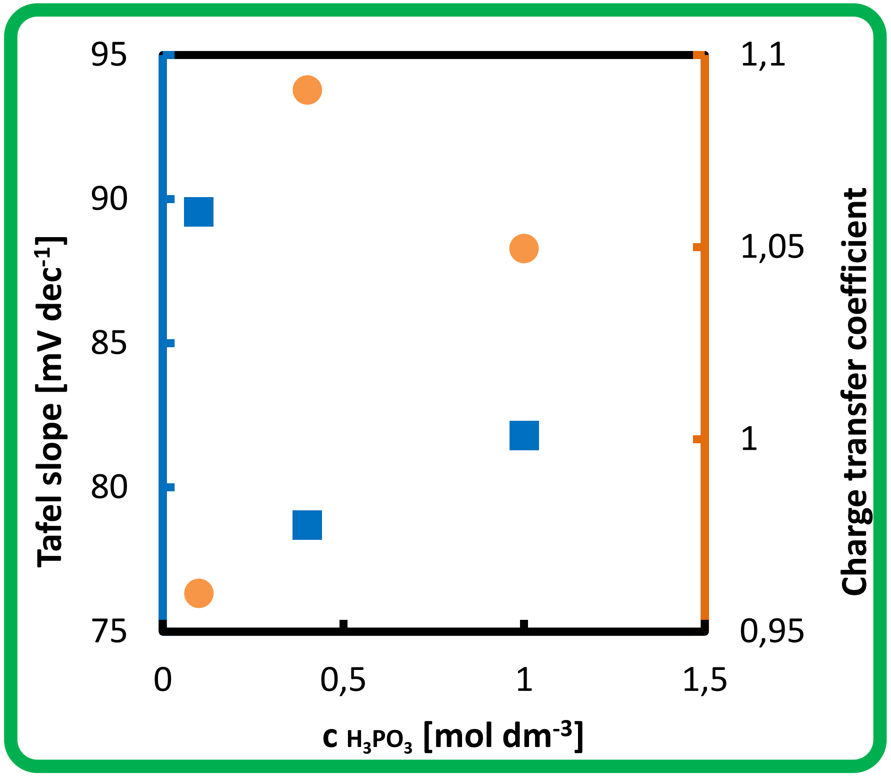
70 °C, 0.5 mol dm^{-3} H_3PO_4



H_3PO_3 oxidation in H_3PO_4 at 160 °C

Preliminary results





Conclusion

Experimental findings:

- H_3PO_3 adsorption on Pt is influenced by tautomeric equilibria
- Mechanism of H_3PO_3 oxidation follows multistep mechanism including chemical steps
- Possible intermediate $H_4P_2O_6$ is oxidized on PtO_x
- ECEC mechanism probably take place with H_3PO_4 as final product
- ECCD mechanism is expected with P (IV) compounds as intermediates

Examination of proposed H_3PO_3 oxidation mechanisms
could enable H_3PO_3 removal during HT PEM FC application

Thank you for your attention!

FCH
FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

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Want to know more?

M. Prokop, T. Bystron, K. Bouzek, Electrochemistry of Phosphorous and Hypophosphorous Acid on a Pt electrode, Electrochimica Acta, 160 (2015) 214-218.