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Impact of electron density on reactions and stability of one-electron oxidized phenyl sulfonates in aqueous solution

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Presently transportation is responsible for nearly a third of greenhouse gas emissions worldwide and is one of the major contributing factors to global warming. [1] Renewable energy sources in combination with electrochemical devices for energy storage have partially been able to mitigate these problems. It is conceivable to replace traditional combustion engines with environmentally friendly fuel cell-based systems that directly convert the chemical energy stored in various fuels into electricity with negligible emissions.

Sulfonated aromatic hydrocarbon-based ionomers are typical constituents of proton exchange membrane fuel cells (PEMFC). Widespread application is currently limited due to their susceptibility to oxidative degradation initiated by $\text{HO}\cdot$, produced in the membrane and electrodes during operation. [2] Degradation involves the formation of highly reactive aromatic cation radicals. [3] These intermediates are Lewis acids that can undergo protolysis equilibria with water and form hydroxycyclohexadienyl radicals and protons. For a given pH, the position of this equilibrium depends on the electron density of the aromatic ring. An equilibrium on the cyclohexadienyl side will increase the degradation rate of the PEM under normal operating conditions. Reduction of the cation radical may lead to repair whereas reduction of the cyclohexadienyl radical will lead to irreversible damage.

In our study, we chose simple alkylated phenyl sulfonates as representatives of PEMs. We were interested in how electron density influences the rates and mechanism of degradation and whether repair *via* one electron reduction is feasible. Therefore, aqueous solutions of model compounds were one-electron oxidized by hydroxyl or sulfate radicals and the reactions were followed by time-resolved UV-Vis spectrometry. These highly oxidizing radicals were produced via pulse radiolysis.

Additionally, continuous irradiation in water with a ^{60}Co source provided radicals at a constant low concentration and allowed us to compare the oxidative stability of the model compounds at different pH values. The degree of degradation was quantified by UPLC-UV/MS. We also studied whether addition of a suitable reductant affected the yield of degradation.

Our findings can be applied to the development of next generation PEMs.

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[2] L. Gubler, S. M. Dockheer and W. H. Koppenol, *J. Electrochem. Soc.*, **158**, B755-B769 (2011).

[3] T. Nemeth, T. de Wild, L. Gubler and T. Nauser, *Phys. Chem. Chem. Phys.*, **24**, 895-901 (2022)

Primary authors: Dr NEMETH, Tamas (Electrochemistry Laboratory, Paul Scherrer Institute); Mr DE WILD, Tym (Electrochemistry Laboratory, Paul Scherrer Institute); Dr GUBLER, Lorenz (Electrochemistry Laboratory, Paul Scherrer Institute); Dr NAUSER, Thomas (Laboratory of Inorganic Chemistry, ETH Zurich)

Presenter: Dr NEMETH, Tamas (Electrochemistry Laboratory, Paul Scherrer Institute)

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