Nanoscale inorganic oxide membranes to enhance the durability of HER-HOR catalysts in H_2-Br_2 flow batteries

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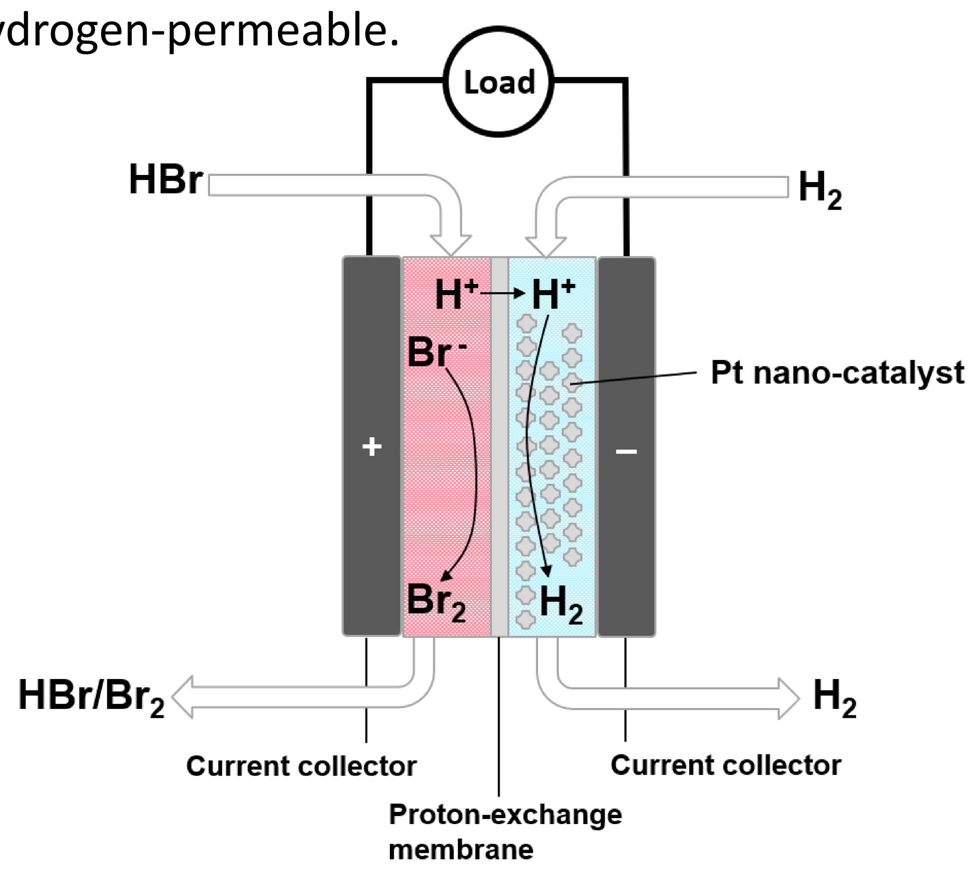
Introduction

Low-cost, large-scale storage of intermittent renewable energy such as solar and wind is an essential component in the energy transition. The H_2-Br_2 redox flow battery is a promising candidate to fulfil this role. However, to decrease the system cost the dissolution resistance of the catalyst for the hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR) needs to be improved. Therein, a balance must be found between catalytic performance, durability, and material cost.

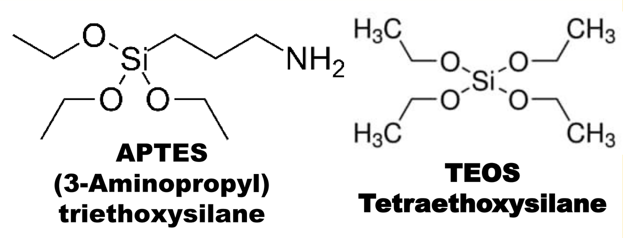
1. Background

In the H_2-Br_2 RFB, the hydrogen reactions are catalyzed by costly Pt nano-catalysts. Bromine species inadvertently crossing through the proton-exchange membrane accelerate the catalyst degradation, leading to shorter battery lifetime and higher system cost. We try to improve upon the catalyst design by encapsulating them beneath thin films of protective metal oxide overlayers (*e.g.*, SiO_2, TiO_2, CeO_x) which selectively block bromine species while being hydrogen-permeable.

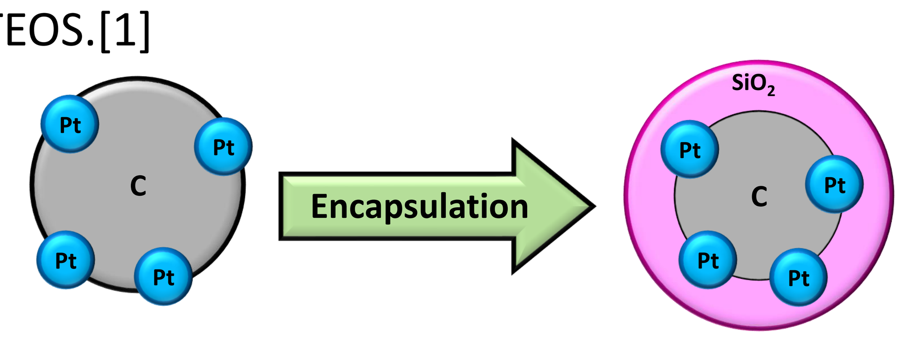


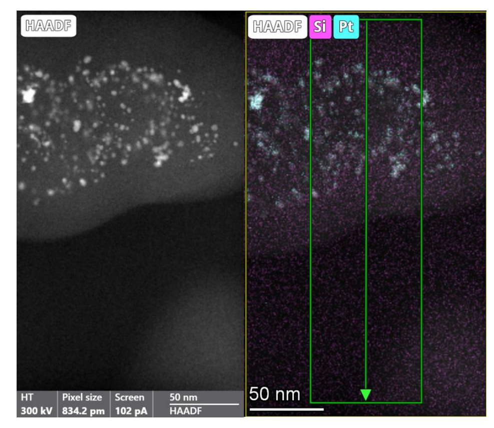
$2\,H^+ + 2\,e^- \rightleftharpoons H_2$	$E^0 = 0.00$ V
$2\,Br^- \rightleftharpoons Br_2 + 2\,e^-$	$E^0 = +1.09$ V
$2\,HBr \rightleftharpoons H_2 + Br_2$	$E^0_{cell} = 1.09$ V

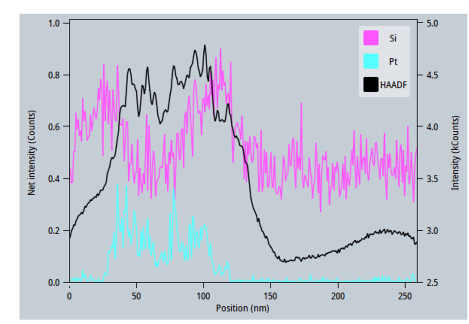
3. Coating of commercial Pt/C



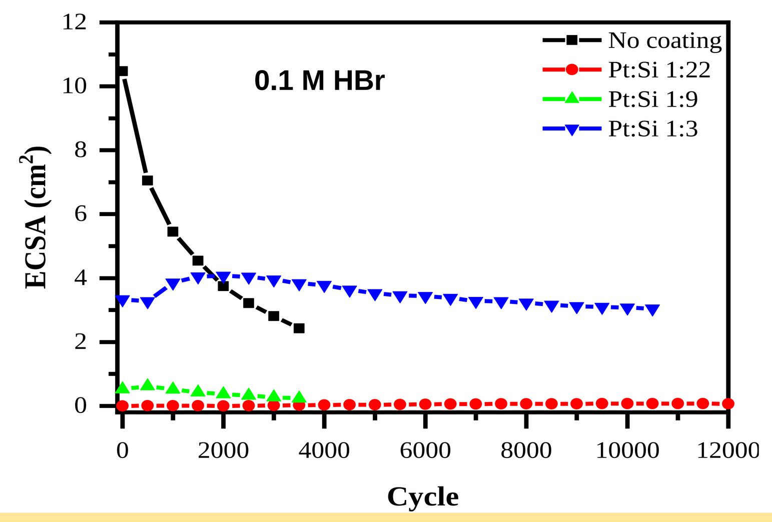
Commercial Pt/C particles were coated with SiO_2 via a chemistry Stöber-like method, based on the successive hydrolysis of APTES and TEOS.[1]

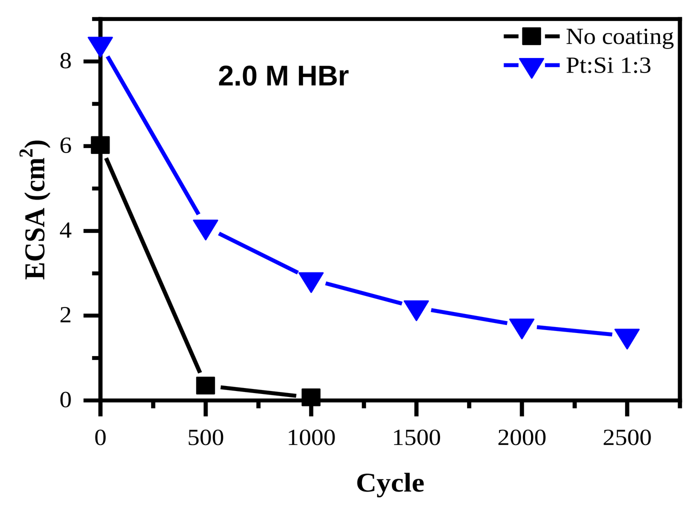






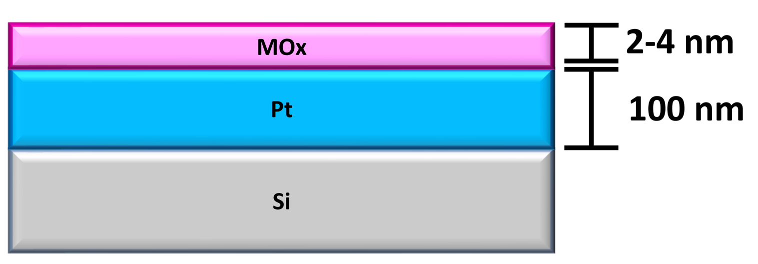
STEM-EDX confirmed the encapsulation of the Pt/C particles with a silica shell. Various Pt:Si ratios (i.e, overlayer thicknesses) were tested by accelerated degradation testing. The decline in electrochemically active surface area (ECSA) during prolonged potential cycling shows that the silica layer slows down catalyst degradation, increasing the half-life by a factor of 12 in 0.1 M HBr and by a factor of 4 in 2.0 M HBr.



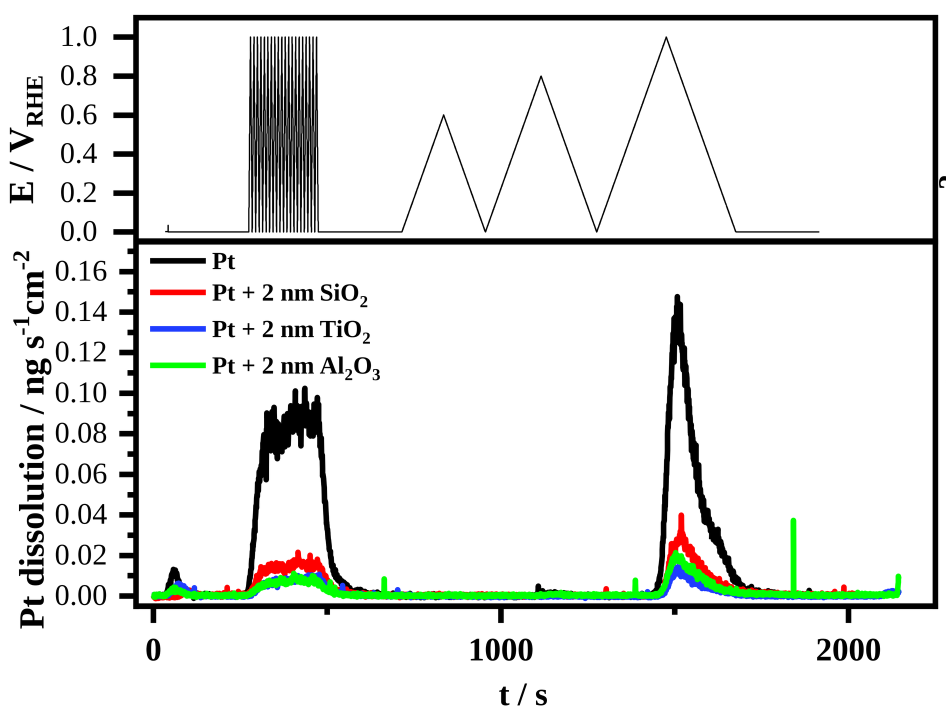


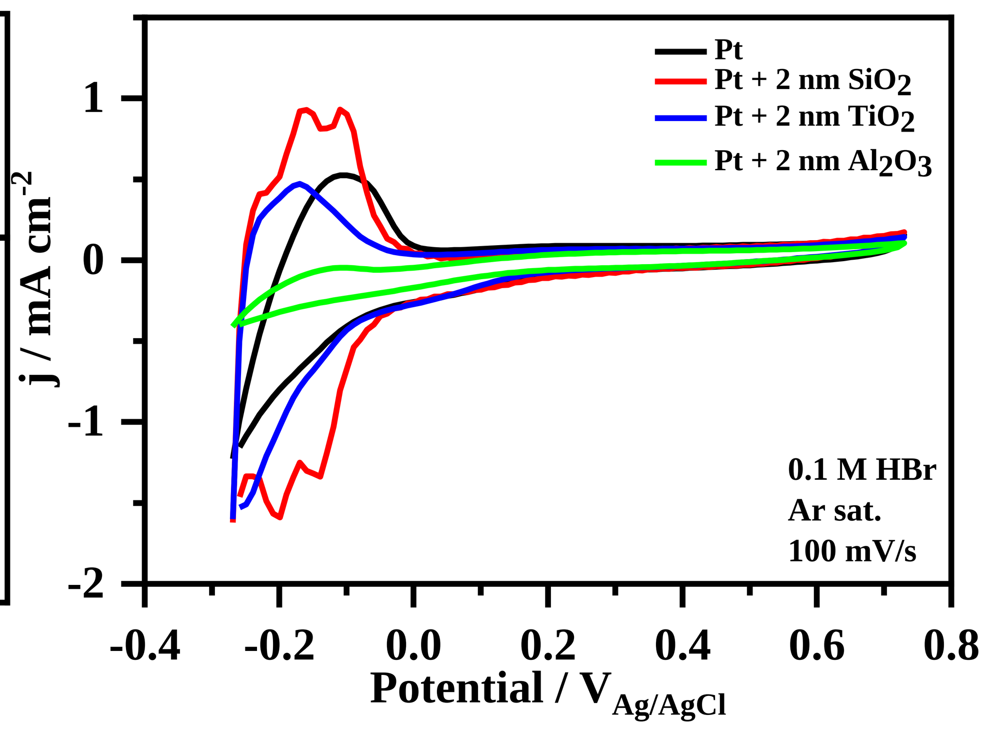
2. Model electrodes

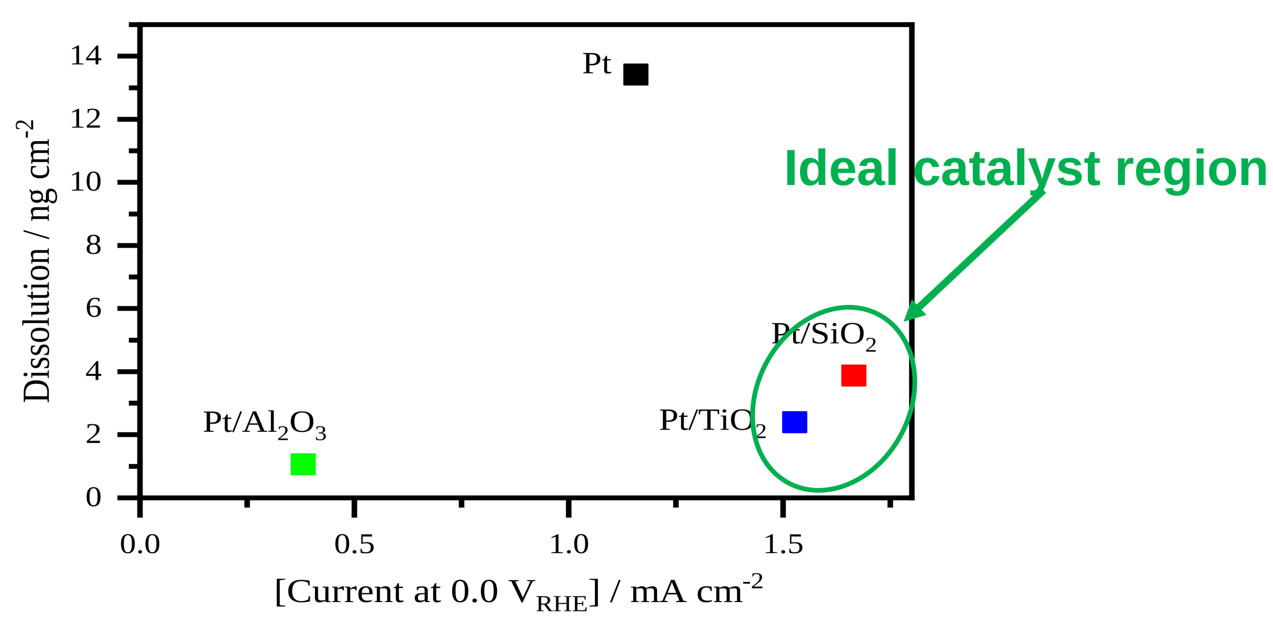
Model electrodes comprising films of Pt sputtered on Si wafers were coated with metal oxide nano-membranes via ALD.



Electrochemistry combined with online ICP-MS was used to quantify the rate of Pt dissolution and study its potential dependence. SiO_2 and TiO_2 were found to restore the typical platinum features seen commonly in weakly adsorbing electrolyte, suggesting that they successfully prevent Br from reaching the platinum surface whilst allowing for hydrogen transport.







4. Conclusions

- Encapsulation of metal catalysts with a few nanometers of oxide coating can improve durability in extremely harsh electrolyte, but fine-tuning is required to find optimal membrane thickness, layer distribution, hydrogen permeability, etc.
- A Pt:Si ratio of 1:3 was found to be optimal for SiO_2/Pt/C catalysts, with a 4-12x improvement in half-life. The enhanced stability quickly makes up for the initial decrease of Pt surface area by preventing Pt dissolution.

References

1. Takenaka, S., et al., *Synthesis of carbon nanotube-supported Pt nanoparticles covered with silica layers.* Carbon, 2008. **46**(2): p. 365-368.
2. Esposito, D. V. (2018). "Membrane-Coated Electrocatalysts—An Alternative Approach To Achieving Stable and Tunable Electrocatalysis." ACS Catalysis **8**(1): 457-465.

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