# Application of Ruthenium complexes in the ammonia electro-oxidation

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For a long time, the scientists are trying to develop water into a cheap, abundant and safe source of hydrogen, thus revolutionising alternative energy field. However, the problems with a high overpotential of the coupled oxygen-evolving reaction (OER), the pH-dependent performance of known catalysts and low stability of catalysts stimulated the development of an alternative approach based on NH<sub>3</sub> splitting. [1]

Ammonia splitting into H<sub>2</sub> and N<sub>2</sub> via ammonia oxidation reaction (AOR), when compared to water splitting, profits from higher thermodynamic favourability and to that related lower energy demands ( $E^0 = 0.092$  V vs  $E^0 = 1.23$  V vs NHE). [1] Further advantages appear when ammonia is compared directly to hydrogen as an energy carrier, as it is liquefiable at only 8 atm. at room temperature while providing 1.5 more hydrogen density than liquid hydrogen itself. [1]

Looking at the similarities between NH<sub>3</sub> and H<sub>2</sub>O chemistry, one can wonder whether OER's catalysts might also be used in AOR. Indeed, recent literature reports provide encouraging reports about the viability of this idea. [2] Herein, we would like to report the results of our study of two different water oxidation catalysts previously developed in our group and recently tested in electrochemical AOR. First, is our original OER RuTda catalyst (Figure 1, left) [3], which mode of action, when compared to literature [4], illustrates the need of the reaching high oxidation numbers at low potentials for good AOR activity. Besides that, we managed to prepare ammonia embedded intermediates and confirm their structure with single-crystal X-ray diffraction. Second discussed family is recently developed oligomeric form of RuBda catalyst (Figure 1, right), which we deposited on the graphitic surface, thus preparing first heterogeneous electrode based on the molecular catalyst for ammonia electro-oxidation. The electrochemical AOR activities of both homogenous (RuTda) and heterogeneous (oligRuBda) systems were then studied under anhydrous conditions as well as in water. Finally, the observed behaviour towards AOR will be discussed in relation to the already known reactivity of these catalysts towards OER.

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### **FIGURES**



Figure 1: Left: RuTda homogeneously electro-catalysed AOR; Right: Heterogenised oligomeric RuBda AOR catalyst

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