Institut für Solarforschung

Sustainable production of ammonia using solar-thermochemical redox cycles

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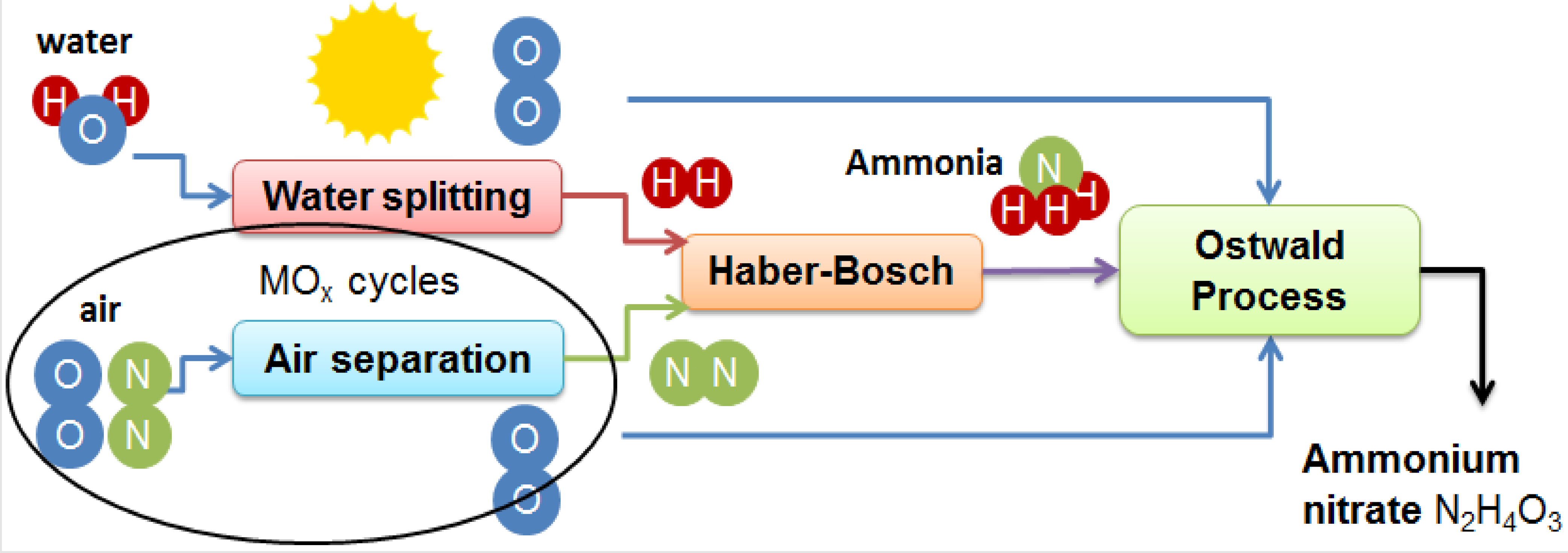


Process schematic for fertilizer production

Motivation

In Project DüSol an innovative process for sustainable fertilizer production is developed and demonstrated. The most important fertilizer and the world's most widely produced chemical, at 184 million ton per year is urea. The precursor of urea production is ammonia, which is synthesized from hydrogen and nitrogen using the Haber-Bosch process. Currently, the required hydrogen and nitrogen are provided by fossil fuels. In 2013, approx. 1.6% of all fossil fuel consumed was generated, in Germany.

So far, no which corresponds to the energy of approx. 2 trillion kWh, which is roughly equivalent to the annual primary energy consumption concept is known, which utilizes solely solar energy directly to produce ammonia from the raw materials water and air can produce. DüSol offers a pioneering approach of coupling two solar-heated thermochemical cycle processes to specifically remove oxygen from gases.

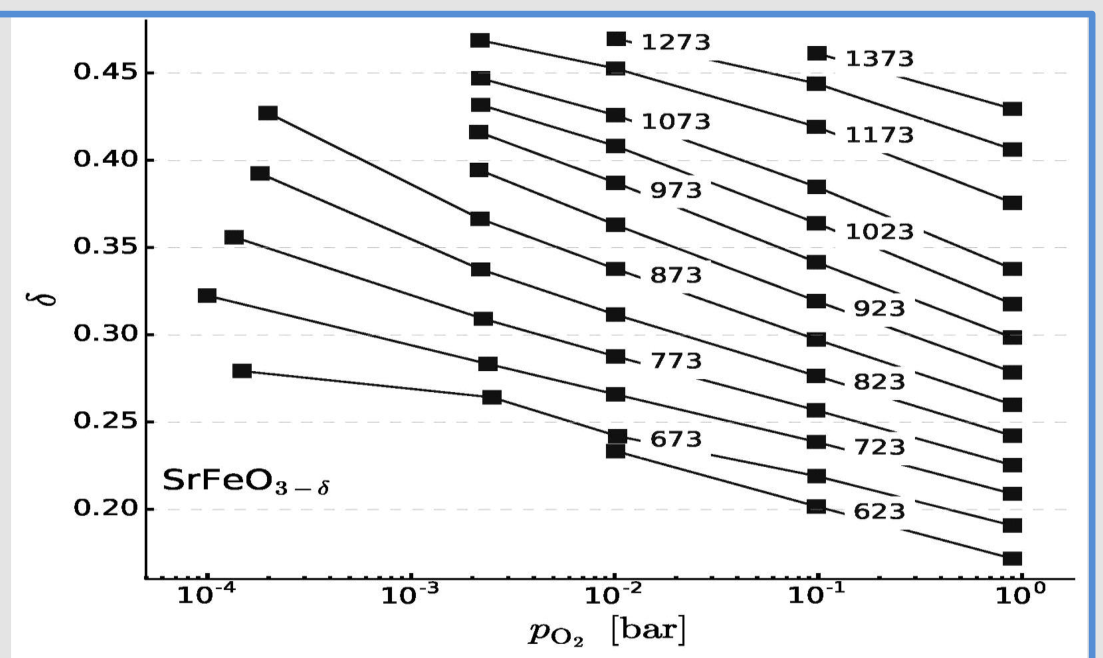
Solar-thermochemical air separation

The re-oxidation step of a redox-cycle can be used to selectively remove oxygen from a gas mixture, therefore provides a mean for nitrogen production from air and for the removal of oxygen impurities from a gas stream.

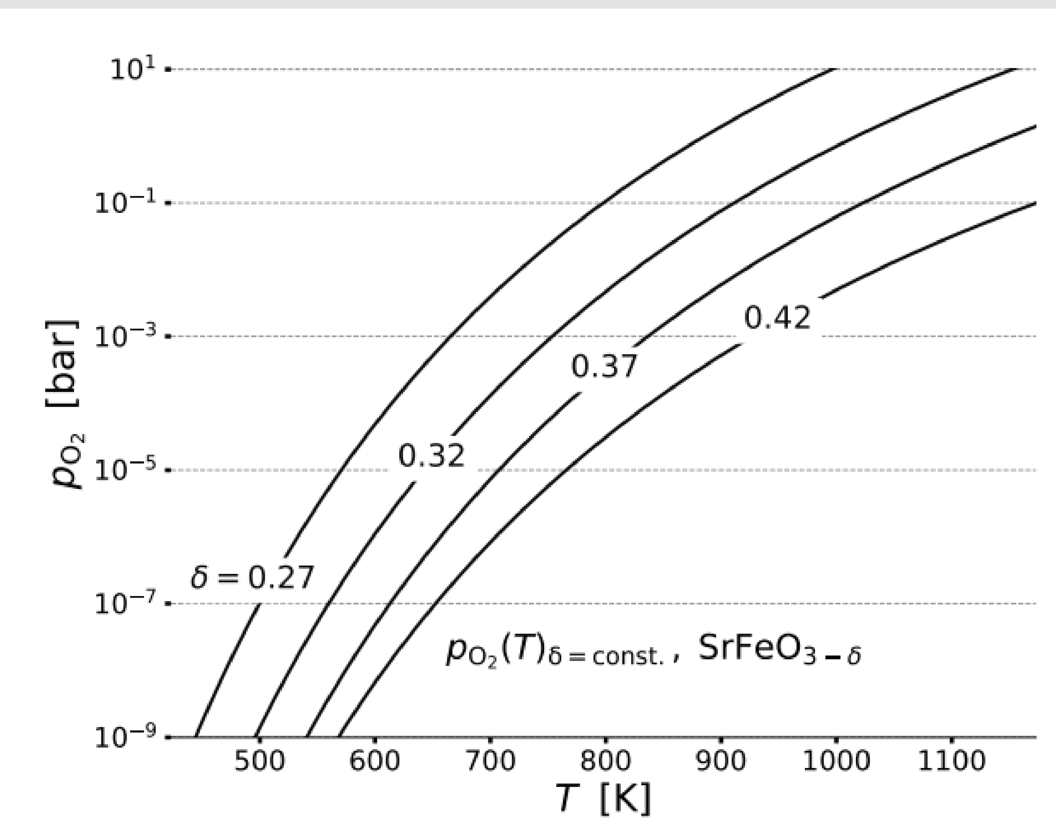
The Haber-Bosch process requires nitrogen with oxygen impurities in the order of ppm. The feasibility of the method is demonstrated by using $SrFeO_x$ perovskite as the redox material, due to ist excellent kinetic properties and cyclability.

The thermodynamics and kinetics of the process were evaluated my means of TGA experiments. The equlilibrium change in stoichiometry δ was determined for a large range of temperatures and oxygen partial pressures. The enthalpy and entropy changes were calculated based on the equilibrium data then they were used to extrapolate the partial pressure to low temperature regions as well.

The result show that by selective oxygen pumping 10^{-5} bar oxygen partial pressure is achievable with less energy demand than mechanical pumping.



Equilibrium oxygen vacancy concentration δ against oxygen partial pressure obtained via thermogravimetric analysis, with data obtained at multiple temperatures labeled in Kelvin



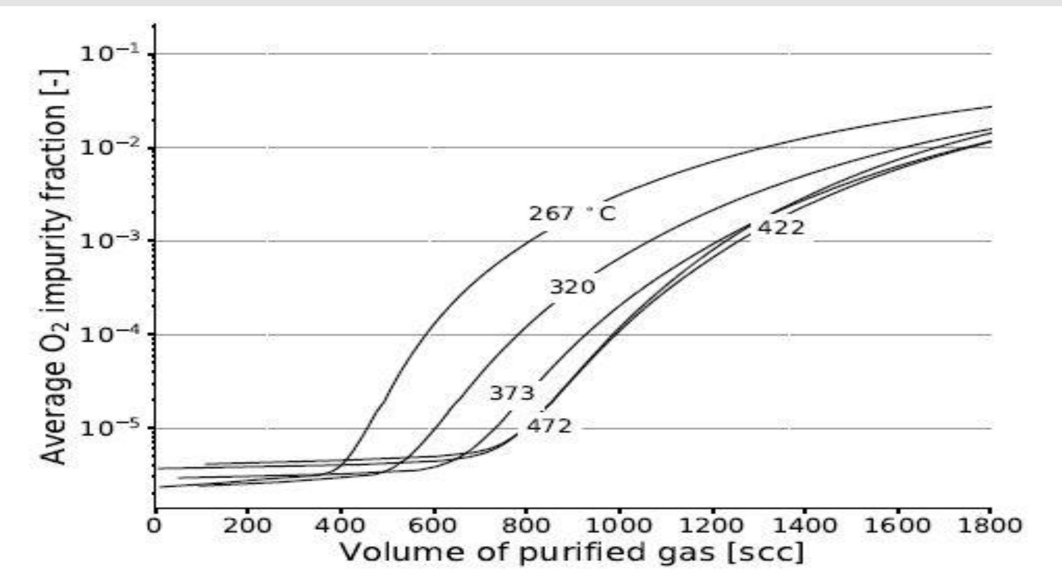
Contours at constant δ showing the oxygen partial pressure vs. temperature obtained using the results of the TGA experiments

Technology demonstration

In order to verify that very low oxygen partial pressures can be achieved, a fixed bed of redox material granules (48 g) were heated and cooled in an infrared furnace under plug flow of argon and synthetic air mixtures.

The oxydation step, where the oxygen removal takes place was performed under different temperatures. The reaction showed very high kinetic activity, furthermore oxygen partial pressures as low as 10^{-6} bar were achieved. The volume of purified gas and the average purity levels at different oxydation temperatures were calculated.

When removing from air, 48 g of material produced 0.602 – 0.662 l of gas with less than 10 ppm of oxygen impurities.



Production curves for cycles performed with varying oxidation temperature

Conclusions and outlook

The results from this work demonstrate the feasibility of using reversible thermochemical redox cycle to achieve low partial pressures of oxygen. The technology demonstation proved that oxygen can be removed from gas streams down to ppm oxygen impurity levels.

In the course of the project the air separation process will be demonstrated in a 20 kW prototype solar reactor

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