ML-driven search for zero-emissions ammonia production materials

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Abstract

Ammonia (NH_3) production is an industrial process that consumes between 1-2% of global energy annually and is responsible for 2-3% of greenhouse gas emissions (Van der Ham et al., 2014). Ammonia is primarily used for agricultural fertilizers, but it also conforms to the US DOE targets for hydrogen storage materials (Lan et al., 2012). Modern industrial facilities use the century-old Haber-Bosch process, whose energy usage and carbon emissions are strongly dominated by the use of methane as the combined energy source and hydrogen feedstock, **not** by the energy used to maintain elevated temperatures and pressures (Pfromm, 2017). Generating the hydrogen feedstock with renewable electricity through water electrolysis is an option that would allow retrofitting the billions of dollars of invested capital in Haber-Bosch production capacity. Economic viability is however strongly dependent on the relative regional prices of methane and renewable energy; renewables have been trending lower in cost but forecasting methane prices is difficult (Stehly et al., 2018; IRENA, 2017; Wainberg et al., 2017). Electrochemical ammonia production, which can use aqueous or steam H_2O as its hydrogen source (first demonstrated ˜20 years ago) is a promising means of emissions-free ammonia production. Its viability is also linked to the relative price of renewable energy versus methane, but in principle it can be significantly more cost-effective than Haber-Bosch (Giddey et al., 2013) and also downscale to developing areas lacking ammonia transport infrastructure (Shipman & Symes, 2017). However to date it has only been demonstrated at laboratory scales with yields and Faradaic efficiencies insufficient to be economically competitive. Promising machine-learning approaches to fix this are discussed.

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1. Why current approaches have failed

Two distinct approaches to electrochemical ammonia production have been demonstrated to date (Kyriakou et al., 2017): fluid electrocatalysis and solid-state ammonia synthesis (SSAS).

Fluid electrocatalysis approaches use aqueous or gaseous mixes of nitrogen, hydrogen (possibly from H_2O) and electrolyte to reduce di-nitrogen to ammonia at catalyzed electrodes. The key challenge has been discovery of electrode catalysts that are preferentially selective for adsorption of nitrogen and its reduction intermediates over adsorption of oxygen or hydrogen (Singh et al., 2016; Foster et al., 2018).

SSAS cells use a solid/polymer ion-conductor membrane to decrease the preferentially selective adsorption requirement: the feedstocks are in separate chambers and the ion-conductor mediates delivery of protons, driven by electrical current. The key challenge has been finding combinations of membrane and electrode materials that have high ammonia yields per area/time, good Faradaic efficiency and that are stable (i.e. don't melt or chemically react) in a given temperature regime (Kyriakou et al., 2017).

In both approaches, relevant materials properties can be approximated from first principles. Relative adsorption energies can be calculated from density functional theory (DFT) (Hoskuldsson et al., 2017). Melting point, ion-conductivity, and reactivity can all be estimated from first principles (Seko et al., 2014; Hong & van de Walle, 2015; Pornprasertsuk et al., 2005; Chermette, 1999). However large scale computational screens have not been performed, due to the relatively large computational cost involved (single-digit CPU-hours for each candidate material and active-surface geometry) coupled with uncertainty about how well first-principles calculations predict reality for any given material class (Pilania et al., 2013).

2. Filling the gap with machine-learning

Machine learning (ML) models have demonstrated they are able to predict small-molecule and materials energies and properties calculated from first-principles (Smith et al., 2017; Gilmer et al., 2017; Xie & Grossman, 2018; Singh et al., 2019). Small molecule equilibrium structures can be auto-regressively generated (Gebauer et al., 2018): demon-

stration of similar for crystal structures modeled as unit cells with periodic boundary conditions is needed because existing random/evolutionary approaches are still quite computationally intensive (Pickard & Needs, 2006; Glass et al., 2006). Rapid property prediction with ML models could enable screening the space of ˜34,000 plausibly stable metal oxides catalogued in the Materials Project (Jain et al., 2013) for suitability as preferentially-selective electrodes.

To our knowledge the electrode catalyst that comes closest to demonstrating economic viability is a doped disordered carbon (Mukherjee et al., 2018), where first-principles calculations done on typical unit-cell sizes miss crucial defect effects. ML can generate tractable, predictive representations of disordered materials (Sharp et al., 2018); such representations should be developed for optimizing preferentially selective adsorption in doped disordered carbons.

As noted by (Kyriakou et al., 2017), a proton conductor in the 250°C and 450°C range could be the missing piece that enables economical SSAS. There are multiple material classes and physical mechanisms of proton conductivity (Nowick & Du, 1995; Quartarone et al., 2017; Tao et al., 2015; Giddey et al., 2013). A pragmatic near-term modeling approach may be to use ML models tailored for each material class and mechanism to predict ion conductivity and stability in that temperature range.

For both fluid electrocatalysts and SSAS materials, the nuisance factors of active-site geometries (Calle-Vallejo et al., 2015) and of optimal unit-cell size to model with (Wang et al., 2010) argue for multi-objective optimization using autoencoders or generative models, similar to those recently developed in drug-discovery research (Gómez-Bombarelli et al., 2018; Jin et al., 2018; Zhou et al., 2018). It is highly recommended to restrict/bias the generator to materials that have plausible synthesis paths, to facilitate experimental verification. An active-learning loop using 3-stage funnel screening (generator → first-principles properties verification → experimental properties verification) is an efficient use of resources in such a search (Aspuru-Guzik & Persson, 2018).

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