

Preview

Jumping Droplets Push the Boundaries of Condensation Heat Transfer

Daniel J. Preston¹ and Evelyn N. Wang^{1,*}

Condensation heat transfer enhancement plays a critical role in more efficient power generation, improved electronics thermal management, and less energy-intensive natural gas processing, among other applications. In this issue of *Joule*, Ronggui Yang and colleagues demonstrated a method to promote jumping droplet condensation on a superhydrophobic surface at unprecedented levels of subcooling while also improving heat transfer performance by up to 100% compared to flat surface coatings. This finding paves the way for future implementation of this technology.

Vapor condensation is routinely used as an effective means of transferring heat or separating fluids for applications ranging from electronic device thermal management¹ to natural gas processing,² refrigeration, and power generation.^{3,4} Filmwise condensation, where the condensed fluid forms a liquid film, is prevalent in typical industrial-scale systems. Conversely, dropwise condensation, where the condensate forms discrete liquid droplets, results in an improvement in heat transfer performance of 4–7× compared to filmwise condensation. More recently, the development of superhydrophobic surfaces has been pursued to enhance condensation heat transfer, where low droplet adhesion and small droplet departure sizes increase the condensation heat transfer coefficient. Specifically, when two or more microscale droplets coalesce on a superhydrophobic surface, they can spontaneously jump away from the surface due to the release of excess surface energy, a phenomenon that has been shown to increase heat transfer by up to 100% compared to that observed during dropwise condensation.^{5,6}

Unfortunately, in past work, increasing the subcooling (the degree to which

the condenser surface is cooled relative to the surrounding vapor) led to nucleation-density-mediated flooding of the condenser surface and degraded the condensation heat transfer performance.⁶ This key limitation for jumping droplet condensation typically occurs when, at elevated subcooling, the spacing between nucleating droplets approaches the lengthscale of the superhydrophobic surface structures; at this point, the surface becomes “flooded” and droplet jumping cannot be sustained. Heat transfer performance degrades due to the added thermal resistance through large pinned droplets adhered to the condensate which has nucleated within surface structures. Jumping droplet condensation had been reported in the literature at up to a subcooling of 6 K, after which flooding occurred.⁵

In this issue of *Joule*, Ronggui Yang and colleagues eliminated the micro-defects that typically form in a network of nanowires, which they hypothesized would eliminate early nucleation-density-mediated flooding.⁷ To do this, they electrochemically grew copper nanowires within an anodic aluminum oxide (AAO) template, which was

purposely fabricated from impure aluminum to allow interconnections between nanowires,⁸ resulting in a 3D interconnected nanowire network on the condenser surface; the 3D nanowire network maintained inter-wire spacing and did not form micro-defects. For comparison, they grew copper nanowires with micro-defects from an AAO template fabricated from 99.999% pure aluminum and also fabricated a flat, hydrophobic copper surface.

Experiments showed that the 3D interconnected nanowire network was able to sustain jumping droplet condensation up to a subcooling of 28 K, an unprecedented result that will enable many new applications for superhydrophobic condenser coatings (Figure 1A). In comparison, the nanowires with micro defects grown in the pristine AAO template flooded at a subcooling of approximately 5 K, in agreement with prior work.⁵ Additionally, as compared to the flat hydrophobic surface, the 3D interconnected nanowire network was able to generate a 100% improvement in heat transfer coefficient over the entire range of subcooling studied.

The results presented in this paper were obtained in the presence of 0.5% noncondensable gases (NCGs). There are many applications where jumping droplet condensation can be used in the presence of NCGs, like dew harvesting and some methods of desalination. However, it is important to note that even 0.5% NCGs can significantly lower the heat flux, particularly at high subcooling, by forming a boundary through which vapor must diffuse;⁹ this phenomenon explains why the reported heat transfer coefficient for

¹Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

*Correspondence: enwang@mit.edu
<https://doi.org/10.1016/j.joule.2018.01.011>



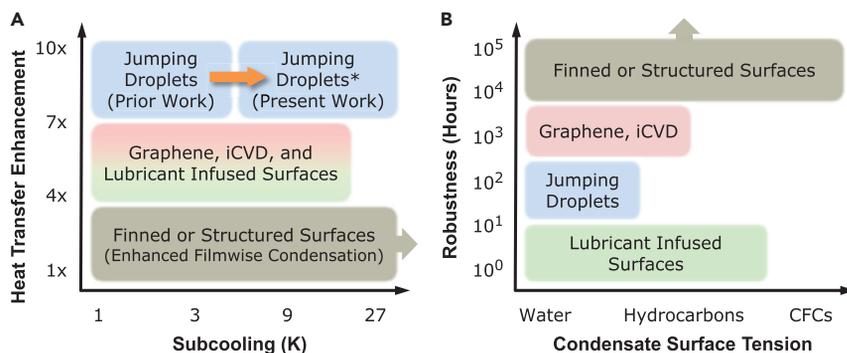


Figure 1. State-of-the-Art Surface Design for Enhanced Condensation Heat Transfer

The condensation heat transfer enhancement achieved by various surface treatments relative to filmwise condensation on a flat surface is shown as a function of subcooling (A). Jumping droplet condensation on superhydrophobic surfaces had claimed the highest heat transfer enhancement, but was limited to low subcooling due to “flooding” of the surface. In this issue of *Joule*, Ronggui Yang and colleagues demonstrated a method to overcome surface flooding and achieve jumping droplet condensation at high subcooling (* indicates presence of noncondensable gas). In light of this work, jumping droplet condensation appears to be unequivocally superior to other methods in terms of heat transfer enhancement; however, it is still limited by its robustness, measured as time until coating failure, and its ability to shed low surface tension condensates (B).

jumping droplet condensation in this work (as low as 15 kW/m²K) is lower than prior reports (100 kW/m²K).⁶ Another important experimental consequence of NCGs accumulating at the surface is that the actual subcooling of the condenser surface relative to the vapor directly adjacent to the surface (which causes flooding) is significantly lower than the subcooling measured relative to vapor far from the surface due to the drop in vapor pressure associated with diffusion through the boundary layer of NCGs. In fact, the actual subcooling relative to the local vapor can be over an order of magnitude lower than the subcooling relative to the far-field vapor¹⁰ as seen in prior work;¹¹ we have added an asterisk to the performance enhancement indicated in Figure 1A to denote that the concentration of NCGs should be considered when interpreting the results in the present work.

In the broader context of surface modification for condensation heat transfer enhancement, two factors limiting widespread implementation of modern approaches are coating robustness (how long a coating can withstand

continuous condensation) and the ability to repel low surface tension fluids (Figure 1B).⁹ In terms of robustness, typical hydrophobic coatings either wear off within days or are so thick and insulating that their thermal resistance offsets any expected improvement. Recent work on thin graphene and initiated chemical vapor deposition (iCVD) coatings demonstrated sustained dropwise condensation of water,^{3,4} but surface designs that maintain filmwise condensation and increase surface area by adding fins or structures currently dominate the market, with the tradeoff that their enhancement is minimal.⁹

Meanwhile, for applications in natural gas processing and refrigeration, condensates are often hydro- or chlorofluorocarbons (CFCs). These low surface tension condensates pose a unique challenge since typical hydrophobic condenser coatings used to shed water often do not repel fluids with lower surface tension. In fact, superhydrophobic surfaces can be worse than chemically identical flat surfaces since surface roughness enhances wettability when the intrinsic contact angle is less than

90°. Lubricant infused surfaces can promote dropwise condensation of hydrocarbons, but currently lack robustness.² Again, surfaces that maintain filmwise condensation but enhance the surface area are effective at improving the heat transfer of even completely wetting fluids and represent the most conservative and widely used surface modification.⁹

The work presented by Ronggui Yang and colleagues in this issue of *Joule* is a significant contribution to jumping droplet condensation that has pushed the boundaries of the field by demonstrating an unprecedented heat transfer enhancement at high subcooling (Figure 1A). We hope to see continued developments to address the other shortcomings of surface engineering for enhanced condensation heat transfer discussed above, namely, coating robustness and shedding of low surface tension fluids, ultimately resulting in energy and cost savings in electric power production, thermal management, natural gas processing, refrigeration, and beyond.

- Oh, J., Birbarah, P., Foulkes, T., Yin, S.L., Rentauskas, M., Neely, J., Pilawa-Podgurski, R.C.N., and Miljkovic, N. (2017). Jumping-droplet electronics hot-spot cooling. *Appl. Phys. Lett.* 110, 123107.
- Preston, D.J., Lu, Z., Song, Y., Zhao, Y., Wilke, K.L., Antao, D.S., Louis, M., and Wang, E.N. (2018). Heat transfer enhancement during water and hydrocarbon condensation on lubricant infused surfaces. *Sci. Rep.* 8, 540.
- Paxson, A.T., Yagüe, J.L., Gleason, K.K., and Varanasi, K.K. (2014). Stable dropwise condensation for enhancing heat transfer via the initiated chemical vapor deposition (iCVD) of grafted polymer films. *Adv. Mater.* 26, 418–423.
- Preston, D.J., Mafra, D.L., Miljkovic, N., Kong, J., and Wang, E.N. (2015). Scalable graphene coatings for enhanced condensation heat transfer. *Nano Lett.* 15, 2902–2909.
- Wen, R., Li, Q., Wu, J., Wu, G., Wang, W., Chen, Y., Ma, X., Zhao, D., and Yang, R. (2017). Hydrophobic copper nanowires for enhancing condensation heat transfer. *Nano Energy* 33, 177–183.
- Miljkovic, N., Enright, R., Nam, Y., Lopez, K., Dou, N., Sack, J., and Wang, E.N. (2013). Jumping-droplet-enhanced condensation on scalable superhydrophobic nanostructured surfaces. *Nano Lett.* 13, 179–187.

- Wen, R., Xu, S., Ma, X., Lee, Y.-C., and Yang, R. (2018). Three-Dimensional Superhydrophobic Nanowire Networks for Enhancing Condensation Heat Transfer. *Joule* 2, this issue, 269–279.
- Wang, W., Tian, M., Abdulagatov, A., George, S.M., Lee, Y.-C., and Yang, R. (2012). Three-dimensional Ni/TiO₂ nanowire network for high areal capacity lithium ion microbattery applications. *Nano Lett.* 12, 655–660.
- Cho, H.J., Preston, D.J., Zhu, Y., and Wang, E.N. (2016). Nanoengineering materials for liquid–vapour phase-change heat transfer. *Nature Materials Reviews* 2, 16092.
- Zhao, Y., Preston, D.J., Lu, Z., Zhang, L., Queeney, J., and Wang, E.N. (2018). Effects of millimetric geometric features on dropwise condensation under different vapor conditions. *Int J Heat Mass Tran* 119, 931–938.
- Ölçeroğlu, E., and McCarthy, M. (2016). Self-Organization of Microscale Condensate for Delayed Flooding of Nanostructured Superhydrophobic Surfaces. *ACS Appl. Mater. Interfaces* 8, 5729–5736.

Preview

Enhancing Catalysis through Substitute-Driven Redox Tuning

Nikolay Kornienko^{1,*}

Electrocatalysts enable many energy conversion and storage technologies. Tuning the electronic structure of electrocatalytic transition metal oxides and complexes by introducing substitute metals—which possess a different electronegativity than the parent metals—presents a rational strategy for enhancing performance. Kuznetsov et al. show a unifying concept regarding how the inductive effects of substitute metals alter the molecular orbital structure of transition metal oxides and complexes. Such tuning leads to increased battery capacity and higher catalytic activity.

The shift to a renewable energy powered society will ultimately be driven by the development of effective methods of energy conversion and storage. Energy is most efficiently stored in chemical bonds, and consequently, energy harvesting and storage often requires bond cleavage and formation. Catalysts speed up these reactions to minimize energy losses and voltage requirements in electrochemical processes. To this end, the discovery of efficient and cost-effective catalysts underpins the growth of technologies ranging from fuel cells and electrolyzers to metal-air batteries.

Oxygen electrocatalysis, whether it be water oxidation in electrolyzers or oxygen reduction in fuel cells, is a kinetically difficult process, and the search for increasingly improved catalysts for these reactions represents a significant bottleneck in energy research. Within

this context, the development of structure-function relationships to understand and subsequently control such materials' electronic character to enhance reactivity is paramount. In this review, Kuznetsov and Han et al. discuss how electronics of transition metal oxides and complexes can be electronically modified through substituting in metals with different electronegativity than the parent metal through inductive effects; that is, through the substitute metal's tendency to withdraw or donate electron density.¹ Importantly, the authors demonstrate how inductive effects similarly function to modify redox behavior of transition metal-based oxide lithium intercalation compounds and oxide oxygen reduction/evolution catalysts as well as molecular materials, therefore elegantly introducing this as a unifying concept across multiple platforms (Figure 1).

The authors first show how heterometal (X) substitution in $[XM_nO_4]^{2-}$ and $[XFe_3O(OH)]^{3-}$ molecular complexes leads to systematic voltage shifts in the electrochemically measured redox center of the bimetallic complexes that scales with the pK_a of the hydrated complex. The pK_a , in this case a measurement of the degree of polarization and ease of cleavage of the O-H bonds, serves as a proxy for the Lewis acidity of substitute X and the degree to which X withdraws electron density from Mn or Fe. To transfer the observations of inductive effects from molecular complexes to heterogeneous electrocatalysts and battery materials, the redox levels and partial density of states (PDOS) of these three classes are aligned on the same absolute energy scale, and the changes to their redox behavior are mechanistically explained by illustrating the induced changes in the degree of separation of bonding and anti-bonding orbitals in the materials' molecular-orbital diagrams. For example, in a transition metal oxide, a metallic substitute with a high degree of Lewis acidity would withdraw electron density away from the parent metal, M, and decrease the covalency of the M-O bond and subsequently shift the redox potential of the M^n/M^{n+1} oxidation positively.

¹Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, UK

*Correspondence: nk485@cam.ac.uk
<https://doi.org/10.1016/j.joule.2018.01.005>

