

Materials enabling nanofluidic flow enhancement

Alan J.H. McGaughey and Davide Mattia, Guest Editors

This issue of *MRS Bulletin* focuses on materials that enable nanofluidic systems with unusually high mass fluxes, termed “enhancement factor” or “slip flow.” There is now ample evidence of such flow enhancement in nanochannels, with sizes ranging from subnanometer to a few nanometers. Most of the studies to date, both experimental and modeling, have focused on carbon nanotubes and, more recently, on graphene. Different fabrication methods result in different structures, surface chemistries, and defects, with a significant effect on flow enhancement. As new one-dimensional and two-dimensional nanomaterials are synthesized, a deeper understanding of the nanoscale transport physics is needed, particularly in the relationship between material properties and flow behavior. Herein, authors at the forefront of experimental, modeling, and theoretical developments in nanofluidic flow describe the state of the art in materials development and characterization.

Introduction

Mass transport through nanoscale pores has been studied for many years in disciplines as diverse as membrane science, soil permeability, and cell physiology. In these fields, emphasis has been placed on the macroscopic outcome, while molecular-level effects on fluid behavior have often been neglected. In the last 10 years, however, the focus has shifted to the effects on fluid behavior of intermolecular interactions between the fluid and the walls of the channel that it flows through. Interest in this field, called nanofluidics, has dramatically increased with the widespread availability of carbon nanotubes (CNTs) and, more recently, graphene, with potential applications to filtration and separation (e.g., water desalination). Initial insights into nanoscale steady-state flow were obtained by numerical simulations,¹ followed by experiments in small membranes of aligned tubes,^{2,3} and measurements of flow through single nanotubes.⁴ These results have been extensively reviewed elsewhere.^{5,6}

A key concept in nanofluidics is flow enhancement, defined as the ratio of the measured flow to an ideal no-slip Poiseuille flow. The latter assumes that the fluid molecules closest to the channel’s surface have zero velocity, in other words, they stick to the surface.^{5,6} Experimental and modeling results have reported flow enhancements ranging from 10 to 100,000 for water flow inside nanotubes made of carbon and other materials.⁶

While a full understanding of the physical origins of flow enhancement has yet to be achieved, some aspects are now generally accepted:

- A 2-nm threshold exists below which the conventional continuum fluid mechanics model can no longer be applied.⁷
- The presence of a reduced viscosity or depletion layer near the tube wall is due to solid–liquid molecular interactions.⁸
- Frictional losses are mainly confined to the entrance region of the nanochannel.⁹

Other aspects are still unclear and represent active areas of research, including the effective dependence of flow enhancement on the nanochannel length; whether a maximum flow enhancement value exists based on the nanochannel’s geometric characteristics and surface chemistry and structure;^{10–13} and the physical state of liquid molecules under nanoscale confinement.¹⁴ For example, water in nanotubes with diameters ranging from 1.1 to 2.1 nm displays strong structural anisotropy. Notably, the diffusivity and viscosity in the axial direction are much larger than in the radial direction, leading to an ordered, helical structure inside a (10,10) CNT.⁷

Nanochannel material and flow enhancement

Experiments and simulations have both shown that the surface structure and chemistry of a nanochannel have a significant

Alan J.H. McGaughey, Carnegie Mellon University, USA; mcgaughey@cmu.edu
Davide Mattia, University of Bath, UK; D.Mattia@bath.ac.uk
doi:10.1557/mrs.2017.60

effect on liquid flow and flow enhancement. Molecular dynamics (MD) simulations have shown that imposing hydrophilic potentials on a CNT structure significantly reduces the flow enhancement,⁸ though a certain amount of slip would still occur.¹⁵ This prediction was confirmed by experimental measurements of small water flow enhancement in hydrophilic alumina nanochannels.¹⁶ While experimental evidence of flow enhancement in nanotubes other than in carbon nanotubes is scarce, more studies have been done with MD, although some results are contradictory. For example, both higher and lower flow enhancements compared to CNTs have been predicted for silicon carbide nanotubes,^{17,18} a material more hydrophilic than carbon. Another interesting example is boron nitride, whose contact angle with water is similar to that of carbon, but for which MD simulations have shown a significantly lower flow enhancement.^{8,18}

A change in flow enhancement can also be obtained by modifying the surface chemistry or structure of the nanochannel. For example, hydrophilic functionalization of CNT tips can ease capillary filling while reducing flow enhancement.¹⁹ A reduction in flow enhancement has also been observed in MD simulations of water flow through CNTs containing defects.²⁰ On the other hand, graphitization of amorphous CNTs changed their wetting behavior from hydrophilic to hydrophobic, inhibiting imbibition, or entry, of water.²¹ Surface modification of CNTs has also been used to control their ability to imbibe liquids other than water, with different polarity or viscosity.²² Similarly, functionalization of CNT tips can be used to control selective permeation of ions through CNT membranes according to MD simulations.²³

These results highlight the strong effect that the properties of wall materials have on flow enhancement in nanochannels. Numerous theoretical models have been developed to account for the strength of solid–liquid interactions on fluid flow, relating the flow enhancement to the wetting behavior via the slip length,²⁴ friction coefficient,¹¹ work of adhesion between the flowing liquid and channel wall,¹³ or reduced fluid viscosity at the wall.²⁵

Fertile ground for experimental and modeling collaborations

Much of the progress in nanofluidics is due to substantial improvements in both experimental and computer simulation methods. Fluid behavior can now be probed in channel sizes on the order of 1–10 nm, where nanoscale confinement effects become important. Nanomaterials can be fabricated with increasing accuracy in terms of size, surface chemistry, and structure, while simulation methods have become powerful enough to produce useful insights at the length scales captured in experimental observations. These advances have resulted in a convergence of experiments and modeling, quickening progress in the field. The articles in this issue highlight the importance of this collaborative process and provide practical steps to achieving this result. On the experimental side, careful design is needed so that

measurements can be directly compared to simulation predictions. This alignment requires control of materials chemistry and structure, as well pore size, particularly in the 1–2 nm range—the region where continuum fluid theory breaks down. On the modeling side, simulations need to be applied consistently and be carefully validated. An example is the porting of interatomic potentials calibrated on the water contact angle at the macroscale to study flow in the interior of a nanochannel.

In this issue

The articles in this issue of *MRS Bulletin* describe the origin of flow enhancement under nanoscale confinement and the design of nanomaterials with tailored enhanced behavior for a range of applications. In his article, Calabrò provides an overview of the material structure and chemistry factors that affect nanoscale flows. Kannam et al. provide a detailed description of the underlying fluid mechanics formulation for describing slip flow, and survey predictions of slip length from atomistic simulations. In their article, Majumder et al. present an overview of experimental efforts to observe enhanced fluid flow in one-dimensional (1D) (e.g., nanotubes) and two-dimensional (2D) (e.g., stacked graphene sheets) nanochannels.

Borg and Reese describe a multiscale modeling framework for predicting the behavior of nanotube membranes at experimental length scales and time scales. Min et al. then detail the characterization of flow in single nanotubes, with focus on measurement platforms and detection techniques. The Corry article describes how nanochannels can be used to control ion transport through the underlying physical mechanisms of size, hydration, and chemical functionalization.

Final considerations

While the concept of flow enhancement is useful to understand the fundamental relationship between channel wall material properties and the flowing liquid, it must be converted into a quantity, such as permeability or permeance, to allow for comparing performance with other porous materials used for filtration. Such a comparison is often hindered by the fact that many studies on flow enhancement in 1D and 2D nanochannels, particularly modeling, do not report the necessary information to calculate permeability or permeance. We hope that this issue will spur readers to provide the necessary information in their future publications to make this comparison possible. These include the channels' and membranes' geometry (channel length and diameter and membrane porosity and tortuosity) and surface chemistry (presence of functional groups or defects), fluid properties (viscosity, density, and temperature), and flow parameters (flow rate or Reynolds number and applied pressure).

References

1. G. Hummer, J.C. Rasaiah, J.P. Noworyta, *Nature* **414**, 188 (2001).
2. M. Majumder, N. Chopra, R. Andrews, B.J. Hinds, *Nature* **438**, 44 (2005).

3. J.K. Holt, H.G. Park, Y. Wang, M. Stadermann, A.B. Artyukhin, C.P. Grigoropoulos, A. Noy, O. Bakajin, *Science* **312**, 1034 (2006).
4. K.V. Agrawal, L.W. Drahushuk, M.S. Strano, *Philos. Trans. R. Soc. Lond. A* **374**, 20150357 (2016).
5. M. Whitby, N. Quirke, *Nat. Nanotechnol.* **2**, 87 (2007).
6. D. Mattia, Y. Gogotsi, *Microfluid. Nanofluid.* **5**, 289 (2008).
7. J.A. Thomas, A.J.H. McGaughey, *Phys. Rev. Lett.* **102**, 184502 (2009).
8. S. Joseph, N.R. Aluru, *Nano Lett.* **8**, 452 (2008).
9. T. Sisan, S. Lichter, *Microfluid. Nanofluid.* **11**, 787 (2011).
10. J.H. Walther, K. Ritos, E. Cruz-Chu, C.M. Megaridis, P. Koumoutsakos, *Nano Lett.* **13**, 1910 (2013).
11. S.K. Kannam, B.D. Todd, J.S. Hansen, P.J. Davis, *J. Chem. Phys.* **138**, 094701 (2013).
12. W. Nicholls, M. Borg, D. Lockerby, J. Reese, *Microfluid. Nanofluid.* **12**, 257 (2012).
13. D. Mattia, F. Calabrò, *Microfluid. Nanofluid.* **13**, 125 (2012).
14. J.A. Thomas, A.J.H. McGaughey, *Nano Lett.* **8**, 2788 (2008).
15. T.A. Ho, D.V. Papavassiliou, L.L. Lee, A. Striolo, *Proc. Natl. Acad. Sci. U.S.A.* **108**, 16170 (2011).
16. K.P. Lee, H. Leese, D. Mattia, *Nanoscale* **4**, 2621 (2012).
17. M. Khademi, M. Sahimi, *J. Chem. Phys.* **135**, 204509 (2011).
18. K. Ritos, D. Mattia, F. Calabrò, J.M. Reese, *J. Chem. Phys.* **140**, 014702 (2014).
19. M. Majumder, N. Chopra, B.J. Hinds, *J. Am. Chem. Soc.* **127**, 9062 (2005).
20. W.D. Nicholls, M.K. Borg, D.A. Lockerby, J.M. Reese, *Mol. Simul.* **38**, 781 (2012).
21. D. Mattia, M.P. Rossi, B.M. Kim, G. Korneva, H.H. Bau, Y. Gogotsi, *J. Phys. Chem. B* **110**, 9850 (2006).
22. M. Majumder, B. Corry, *Chem. Commun.* **47**, 7683 (2011).
23. B. Corry, *Energy Environ. Sci.* **4**, 751 (2011).
24. C. Neto, D.R. Evans, E. Bonaccorso, H.-J. Butt, V.S.J. Craig, *Rep. Prog. Phys.* **68**, 2859 (2005).
25. J.A. Thomas, A.J.H. McGaughey, O. Kuter-Arnebeck, *Int. J. Therm. Sci.* **49**, 281 (2010). □



Alan McGaughey is a professor of mechanical engineering at Carnegie Mellon University (CMU) and a Fellow of The American Society of Mechanical Engineers. He earned a B.Eng. degree in mechanical engineering from McMaster University, Canada, in 1998, a M.A.Sc. degree in mechanical and industrial engineering from the University of Toronto, Canada, in 2000, and a PhD degree in mechanical engineering from the University of Michigan in 2004. He was a Harrington Faculty Fellow at the University of Texas at Austin from 2012 to 2013, was awarded CMU's Teare Teaching Award in 2014, and was named an Outstanding Referee by the American Physical Society in 2015. His research focuses on the modeling of nanoscale transport phenomena. McGaughey can be reached by phone at 412-268-9605 or by email at mcgaughey@cmu.edu.



Davide Mattia is a professor of chemical engineering at the University of Bath, UK. He earned a MSc degree in materials engineering from the University of Naples Federico II, Italy, in 2002, and a PhD degree in materials science and engineering from Drexel University in 2007. He is a chartered engineer; a Fellow of the IChemE; and a past Royal Academy of Engineering research fellow. His research interests focus on the development of novel one- and two-dimensional hybrid membranes for water-treatment processes and understanding the effects of nanoscale confinement on fluid flow. Mattia can be reached by phone at +44 (0) 1225 383961 or by email at D.Mattia@bath.ac.uk.



RESPIRABLE SILICA (ALPHA QUARTZ) MEASUREMENTS



Crystalline silica is a very common, naturally occurring mineral consisting of silicon and oxygen. Differences in temperature and pressure can cause the atomic structure to change, creating polymorphs of silica. These are commonly known as alpha quartz, beta quartz, cristobalite and tridymite. X-ray diffraction is an excellent analytical technique for the detection of crystalline silica, more accurate than many other methods due to its ability to distinguish between the different polymorphic phases.

This is accomplished by measuring a series of known concentrations of quartz sample. These are fast scans over selected regions so the data collection times are short. The data collected on the Rigaku MiniFlex™ is shown in Figure 1. In this case, samples from 10 to 40 micrograms were used to create the calibration curve. The non-linear fit is shown in Figure 2.

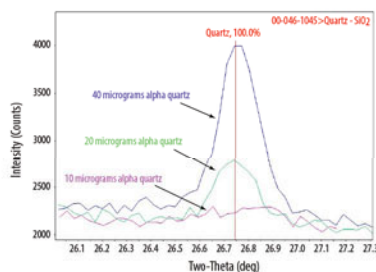


Figure 1

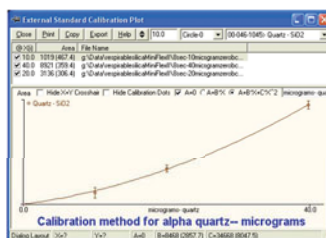


Figure 2



APP BYTE

Rigaku Corporation and its Global Subsidiaries
www.Rigaku.com | info@Rigaku.com



2017 Volume 7, Issue 1

PROSPECTIVES

Are lead-free piezoelectrics more environmentally friendly?

T. Ibn-Mohammed, S.C.L. Koh, I.M. Reaney, and D.C. Sinclair, The University of Sheffield, UK; **K.B. Mustapha**, The University of Nottingham, Malaysia; **A. Acquaye**, University of Kent, UK; and **D. Wang**, The University of Sheffield, UK

Considered as a less hazardous piezoelectric material, potassium sodium niobate (KNN) has been in the fore of the search for replacement of lead (Pb) zirconate titanate for piezoelectrics applications. Here, we challenge the environmental credentials of KNN due to the presence of ~60 wt% Nb_2O_5 , a substance much less toxic to humans than lead oxide, but whose mining and extraction cause significant environmental damage. DOI:10.1557/mrc.2017.10

Three-dimensionally printed cellular architecture materials: perspectives on fabrication, material advances, and applications

Manpreet Kaur, Simon Fraser University, Canada; **Seung Min Han**, Korea Advanced Institute of Science & Technology, Korea; and **Woo Soo Kim**, Simon Fraser University, Canada

Three-dimensional (3D) printing generates cellular architected metamaterials with complex geometries by introducing controlled porosity. Their ordered architecture, imitative from the hierarchical high-strength structure in nature, defines the mechanical properties that can be coupled with other properties such as the acoustic, thermal, or biologic response. Recent progress in the field of 3D architecture materials have advanced that enables for design of lightweight materials with high strength and stiffness at low densities. Applications of these materials have been identified in the fields of ultra-lightweight structures, thermal management, electrochemical devices, and high absorption capacity. DOI:10.1557/mrc.2016.62

FUNCTIONAL OXIDES PROSPECTIVES

Self-assembly of nanostructures with multiferroic components using nucleic acid linkers

Ferman A. Chavez and **Gopalan Srinivasan**, Oakland University, USA

Self-assembly of multiferroic oxide composites by chemical and biochemical methodology is discussed. The approach involves covalently attaching organic functional groups or oligomeric DNA/RNA to the nanoparticles (NPs). The organic functional groups are only reactive toward functional groups located on different NPs. Using oligomeric DNA/RNA, one could program NPs to only interact with particles possessing complementary DNA/RNA. We have applied both concepts to the assembly of nanostructures with ferrites for the ferromagnetic phase and barium titanate for the ferroelectric phase. The assembled core-shell particles and superstructures obtained in a magnetic field show evidence for strong interactions between the magnetic and ferroelectric subsystems. DOI:10.1557/mrc.2016.63

Opportunities in vanadium-based strongly correlated electron systems

Matthew Brahlek, Lei Zhang, Jason Lapano, Hai-Tian Zhang, and Roman Engel-Herbert, The Pennsylvania State University, USA; **Nikhil Shukla** and **Suman Datta**, University of Notre Dame, USA; and **Hanjong Paik** and **Darrell G. Schlom**, Cornell University, USA

The diverse and fascinating properties of transition metal oxides stem from the strongly correlated electronic degrees of freedom; the scientific challenge and range of possible applications of these materials have caused fascination among physicists and materials scientists, thus capturing research efforts for nearly a century. Here, we focus on the binary V_xO_y and the ternary perovskite AVO_3 and review the key aspects from the underlying physical framework and their basic properties, recent strides made in thin-film synthesis, to recent efforts to implement vanadium-based oxides for practical applications that augment existing technologies, which surpass limitations of conventional materials. DOI:10.1557/mrc.2017.2

FUNCTIONAL OXIDES RESEARCH LETTER

X-ray spectroscopies studies of the 3d transition metal oxides and applications of photocatalysis

Yifan Ye and **Mukes Kapilashrami**, Lawrence Berkeley National Laboratory, USA; **Cheng-Hao Chuang**, Tamkang University, Taiwan; **Yi-sheng Liu** and **Per-Anders Glans**, Lawrence Berkeley National Laboratory, USA; and **Jinghua Guo**, University of California, Santa Cruz and Lawrence Berkeley National Laboratory, USA

Recent advances in synchrotron based x-ray spectroscopy enable materials scientists to emanate fingerprints on important materials properties, e.g., electronic, optical, structural, and magnetic properties, in real-time and under nearly real-world conditions. This characterization in combination with optimized materials synthesis routes and tailored morphological properties could contribute greatly to the advances in solid-state electronics and renewable energy technologies. In connection to this, such perspective reflects the current materials research in the space of emerging energy technologies, namely photocatalysis, with a focus on transition metal oxides, mainly on the Fe_2O_3 - and TiO_2 -based materials. DOI:10.1557/mrc.2017.6

RESEARCH LETTERS

Spray pyrolysis and electrochemical performance of $\text{Na}_{0.44}\text{MnO}_2$ for sodium-ion battery cathodes

Kuan-Yu Shen, Miklos Lengyel, Louis Wang, and Richard L. Axelbaum, Washington University in St. Louis, USA

In this study, we investigate spray pyrolysis as an approach to synthesis of tunnel structure sodium manganese oxide, as it is a cost-effective and scalable technology. The powders synthesized with Na/Mn ratio of 0.50 displayed a pure tunnel structure, and demonstrated the best electrochemical performance, with a discharge capacity of 115 mAh/g. The material also showed good cycleability and rate capability. Noticeable decay in performance was seen in materials with Na/Mn ratios other than 0.50, indicating that this material is sensitive to minor compositional deviations. This study has demonstrated that spray pyrolysis is a promising synthesis method for this material. DOI:10.1557/mrc.2017.4

On single-phase status and segregation of an as-solidified septenary refractory high entropy alloy

Boliang Zhang and Yang Mu, Louisiana State University, USA; M.C. Gao, National Energy Technology Laboratory & AECOM Corporation, USA; W.J. Meng and S.M. Guo, Louisiana State University, USA

Phase predictions and characterizations on as-solidified septenary refractory high-entropy alloy, CrMoNbReTaVW, are presented. The simulated solidification process predicts a single body-centered-cubic (BCC) crystal structure with the tendency of compositional segregation. X-ray diffraction results confirm the “single-phase-like” BCC structure, while further experimental characterizations reveal the existence of multiple grains with significantly different compositions yet the same crystal structure and similar lattice. DOI:10.1557/mrc.2017.7

Electrospun carbon nanofiber coated with rambutan-like NiCo_2O_4 microspheres as electrode materials

Hua Chen, Zhejiang Sci-Tech University, China; Guohua Jiang, Zhejiang Sci-Tech University, National Engineering Laboratory for Textile Fiber Materials and Processing Technology, and Ministry of Education, China; and Weijiang Yu, Depeng Liu, Yongkun Liu, Lei Li, and Qin Huang, Zhejiang Sci-Tech University, China

The novel three-dimensional rambutan-like NiCo_2O_4 microspheres have been successfully coated onto a surface of carbon nanofibers (CNFs) to form NiCo_2O_4 -CNFs hybrids. The composition and microstructure of NiCo_2O_4 -CNFs were characterized by the field-emission scanning electron microscopy, x-ray photoelectron spectroscopy, transmission electron microscopy, and x-ray diffractometer. The obtained NiCo_2O_4 -CNFs exhibited a specific capacity of 160 mAh/g at 1 mA/cm² in 2 M potassium hydroxide aqueous solution. The specific capacity gradually increases with the increasing of cycles; and after 3000 cycles, the specific capacity still remains over 90%. DOI:10.1557/mrc.2017.11

Selective laser melting of TiC/H13 steel bulk-form nanocomposites with variations in processing parameters

Bandar AlMangour, Franklin Yu, and Jenn-Ming Yang, University of California, Los Angeles, USA; and Dariusz Grzesiak, West Pomeranian University of Technology, Poland

TiC/H13 nanocomposite parts were processed by selective laser melting using various energy densities; one part also underwent hot isostatic pressing (HIP). The effect of energy density and HIPing on densification, microstructure, and hardness were evaluated. It was found that the densification was not largely affected by the energy density, but the HIP-treated sample displayed a large improvement in relative density. With increasing energy density, the microstructures showed high levels of dispersion of nanoparticles, while HIP treatment coarsened the microstructure and induced agglomeration. Both HIP treatment and increased energy density lowered hardness markedly; this was likely due to annealing effects. DOI:10.1557/mrc.2017.9

Diketopyrrolopyrrole-based polymer:fullerene nanoparticle films with thermally stable morphology for organic photovoltaic applications

Natalie P. Holmes, University of Newcastle, Australia; Ben Vaughan, University of Newcastle and CSIRO Energy Technology, Australia; Evan L. Williams, Agency for Science, Technology, and Research (A*STAR), Singapore; Renee Kroon and Mats R. Andersson, University of South Australia, Australia and Chalmers University of Technology, Sweden; A.L. David Kilcoyne, Lawrence Berkeley National Laboratory, USA; Prashant Sonar, Agency for Science, Technology, and Research (A*STAR), Singapore and Queensland University of Technology, Australia; and Xiaojing Zhou, Paul C. Dastoor, and Warwick J. Belcher, University of Newcastle, Australia

Polymer:fullerene nanoparticles (NPs) offer two key advantages over bulk heterojunction (BHJ) films for organic photovoltaics (OPVs), water-processability and potentially superior morphological control. Once an optimal active layer morphology is reached, maintaining this morphology at OPV operating temperatures is key to the lifetime of a device. Here we study the morphology of the PDPP-TNT (poly{3,6-dithiophene-2-yl-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-*alt*-naphthalene}):PC₇₁BM ([6,6]-phenyl C₇₁ butyric acid methyl ester) NP system and then compare the thermal stability of NP and BHJ films to the common poly(3-hexylthiophene) (P₃HT): phenyl C₆₁ butyric acid methyl ester (PC₆₁BM) system. We find that material T_g plays a key role in the superior thermal stability of the PDPP-TNT:PC₇₁BM system; whereas for the P₃HT:PC₆₁BM system, domain structure is critical. DOI:10.1557/mrc.2017.3