Program and Book of Abstracts

International Workshop on Mechanics of Energy Materials
(IWMEM 2016)

Edited by
Dr. Yixiang Gan
Dr. Gwénaëlle Proust
Dr. Laurence Brassart
Dr. Ratna Kumar Annabattula

14-15 November 2016, The University of Sydney
Venue and Map

The Darlington Centre, The University of Sydney.

Location: 174 City Road, Darlington NSW 2008. Phone: +61 (0)2 93514664
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| Lunch | 12:30 – 13:40 |

| Open Discussion | 13:40 – 15:00 |

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Phase-field modeling of phase changes and fracture in electrode particles of lithium ion batteries

Magalie Huttin, Markus Klinsmann, Tao Zhang, and Marc Kamlah

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Meanwhile, it is generally accepted that mechanical properties and processes influence performance and degradation of electrochemical storage systems such as lithium ion batteries (LIB). In this talk, we consider the interaction of mechanics and diffusion in individual electrode particles.

Most host materials for electrochemical energy storage show phase changes upon intercalation. By phase-field modeling we study the effect of phase changes on the generation of mechanical stresses in electrode particles.

Coupling the fourth order Cahn-Hilliard partial differential equation (PDE) for the species concentration to small and finite deformations mechanics [1] shows the occurrence of large stresses due to the strain mismatch caused by phase segregation [2]. Even for spherical geometries under spherically symmetric boundary conditions, imposing any symmetries on the solution is shown to possibly exclude states of minimum energy, which, for example, questions the so-called core shell scenario often adopted to simplify modeling (Fig. 1).

![Fig. 1: Non-spherical concentration distribution in a spherical particle under spherically symmetric boundary conditions](image-url)
To avoid the numerical difficulties involved with the Cahn-Hilliard equation, an alternative approach has been introduced which, besides the conventional species concentration, introduces the so-called non-local species concentration. This quantity is governed by a Helmholtz-type PDE resulting in a theory governed by two coupled second order PDEs [3]. Recently, this approach has been adopted for the simulation of phase segregation in electrode particles of LIB [4]. We compare the two approaches in terms of results and computational cost.

Furthermore, a phase-field approach to fracture is used to simulate mechanical particle damage caused by stresses during charging and discharging processes. In this modeling approach, failure is described by a phase-field $d$ which assumes zero values in intact material while locations with values of $d$ approaching unity represent cracked material. This continuous phase-field is governed by a second order PDE [5, 6]. In our case, it has been coupled to mechanics while the mechanical fields are coupled to species concentration [7, 8]. We discuss crack growth in electrode particles and breakage during insertion and extraction cycles. In this context, regimes of no failure, as well as stable and unstable crack growth have been identified, where in the latter case it is important to consider inertia effects.

References:

Modelling chemo-mechanical couplings in high-capacity electrodes for Li-ion batteries

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Lithium-ion batteries operate by cyclically inserting lithium into, and extracting lithium from, solid electrodes. During charge and discharge of a Li-ion battery, the amount of Li in the electrodes varies substantially, causing the host electrode to deform. For instance, Silicon, a promising high-capacity anode material, may undergo up to 300% volume expansion accompanied by severe structural change. When constrained, these large deformations induce significant stresses that may in turn cause mechanical degradation of the electrode, resulting in capacity fading after several cycles of lithiation and delithiation. Stresses also affect the kinetics of reaction and diffusion of lithium into the host material in a significant way. Understanding the complex relationship between mechanics and chemistry in electrode materials is crucial for designing batteries with improved cycle life and reliability.

This work focuses on the development of continuum-mechanics models that couple deformation, lithium diffusion and chemical reactions in high-capacity electrodes. Our main objective is to gain a better insight of the coupled chemical-mechanical effects underlying the behaviour of electrode materials during lithiation. A first study addresses the lithiation of crystalline nanopillars, which involves the formation of an amorphous LixSi layer (x≈3.75) that progresses toward the interior of the nanopillars. The migration rate of the lithiated layer is limited by the amorphisation reaction, rather than by Li diffusion. On the other hand, the migration rate strongly depends on the crystallographic orientation, resulting in anisotropic swelling behaviour. In a recent study [1], we investigated the effect of metallic coating on the swelling and fracture behaviour of nanopillars, both experimentally and numerically. Coated structures display different swelling and fracture regimes depending primarily on the
coating thickness to pillar diameter ratio. For low ratios, swelling and cracking are anisotropic, although with different fracture sites compared to uncoated nanopillars. The swelling behaviour progressively becomes isotropic when the ratio increases, which is attributed to the large stress-induced slowing down of the reaction kinetics.

Fig. 1: Stress-composition curve during cyclic lithiation of a thin-film Si electrode. The model captures chemo-mechanical softening characterized by a lower effective flow stress as compared to the flow stress measured during purely mechanical loading.

A second study focuses on lithiation-assisted plasticity of amorphous silicon. Specifically, silicon demonstrates remarkable softening when subject to a combined chemo-mechanical loading, as compared to mechanical loading alone [2], and this softening cannot be captured by classical von Mises plasticity. We developed a new chemo-mechanical plasticity that generalizes the von Mises plasticity theory by including a contribution of the chemical driving force in the definition of the equivalent stress [3]. The model was used to simulate several homogeneous states of deformation in amorphous Si electrodes subjected to chemical and mechanical loads. For an electrode under vanishingly small stress and current, cyclic lithiation and delithiation causes hysteresis in the chemical potential-concentration curve. The hysteresis is attributed to the energy barriers needed to break and reform atomic bonds during lithiation. For a thin-film electrode bonded to a substrate, cyclic lithiation and delithiation causes hysteresis in both the voltage-concentration curve and the stress-concentration curve [4]. The coupled chemical-mechanical plasticity model predicts significant lithiation-induced softening, as compared to the plastic response of amorphous Si under pure mechanical
loading. Model predictions agree reasonably well with experimental data (Fig. 1). Additional experimental results are needed to further validate and refine the theory.

References


Nano-carbons-functionalized polythiophene based hybrid electrode materials for applications in high-performance energy storage devices

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Organic conjugated polymers have potential applications in electronic and opto-electronic devices due to their low cost, resistant to chemicals, environmental stability, controlling of doping-dedoping processes, flexible film forming property, convenient to modify polymer structure, highly sensitive to a broad range of analytes, excellent thermal, mechanical, catalytic electrical and electro-chemical properties. They can find applications in various fields such as energy storage and energy conversion systems (batteries, supercapacitors, fuel cells and solar cells), LEDs, sensors (chemical, biological and gas), transistors, and biomedical devices. However, very limited progress has been made in polythiophene/nano-carbons (3D graphene nanosheets, carbon fiber fabric)-based functional nanohybrid electrode materials for low cost and high-performance electro-chemical energy storage device (batteries and supercapacitors) applications. In this work, 3D graphene nanosheets and flexible carbon fiber fabric are functionalized with the series of thiophene-based polymers (e.g. poly(3,4-ethylenedioxythiophene), polyhexylthiophene, etc) through the self-assembly and chemical oxidative polymerization techniques to fabricate nano-carbons/polythiophene based polymeric functional nanohybrid electrochemical devices. Obtained novel graphene/polythiophene or carbon fiber fabric/polythiophene based electrode materials showed excellent electro-chemical performance than that of pure graphene nanosheets and carbon fabric. They showed excellent specific capacitance with over 90% of coulombic efficiency and cycling stability after 2000 cycles, indicates that they are excellent electrodes for the high performance supercapacitors.
Mechanical Measurements on Electrode Materials for Lithium-Ion Batteries

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Lithium-ion batteries are commonly used to power small electrical devices and are of increasing importance for grid scale applications where they can buffer the fluctuating energy supply and demand in the electrical grid. For these applications, the long term reliability is of very high importance. The repeated insertion and removal of lithium into/from the electrodes leads to inevitable mechanical stresses that interact with the electrochemical processes and affect the reliability of a battery. In order to investigate such mechanical effects, we have used in situ substrate curvature experiments and scanning electron microscopy. In this presentation, the mechanically induced degradation of a positive electrode will be exemplified using LiMn2O4. Here severe mechanical damage and capacity loss was found after 1000 cycles. The evolution of the damage as investigated by SEM will be reported. The degradation mechanism can be inferred from the combination of SEM and mechanical stress data. Mechanical effects can be particularly strong in high capacity materials for negative electrodes. Here, the mechanical stress data provided by substrate curvature measurements not only helps in assessing reliability but also can be used in conjunction with the electrochemical data to study reaction pathways. In this context, the lithium induced crystallization and amorphization of germanium electrodes were investigated using mechanical stress as a probe for the underlying electrochemical processes. In silicon and germanium film electrodes, mechanical stresses and plastic flow cause strong changes in electrode morphology. We will show how mechanical constraints can suppress such processes and improve the reliability of high capacity electrodes.
Coupled stress-diffusion effects on the chemo-mechanical response of an elastic body with geometric discontinuities

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Diffusion of hydrogen into metals is a well-known phenomena and its influence on the strength has been studied extensively in the literature through various models [1]. Similarly, the diffusion of lithium ions into graphite electrodes [2] and the associated implications have been studied in the literature. In this work, we present a fully coupled chemo-mechanical framework for simulating the effects of two-way interaction between diffusion and stresses in an isotropic elastic body with discontinuities. A comparative study of the one-way coupling (diffusion to stress only) and two-way coupling (diffusion and stress interact with each other) is presented. In particular, the influence of the size and shape of the geometric discontinuities on the chemo-mechanical response of the system will be discussed. The geometry of the model system chosen for this study consists of an elastic plate with two holes separated by a distance H and U as shown in Fig. 1.

The plate is constrained to move in x direction on the left edge and the displacement in y direction is also constrained at the center point on the left edge. The plate is subjected to a uniform axial displacement \( u_x = 0.01 \) m on the right edge and held at that position. At initial concentration \( c = 0 \) in the entire domain except on the left edge where it is prescribed as \( c_0 = 1 \). The transient diffusion equation taking into account of the influence of the gradient of the hydrostatic stress is solved simultaneously with the elastic equilibrium equation. The evolution of concentration with time at 6 critical points (see marked circles in Fig. 1) for different geometric configurations is investigated. The material properties of the system are taken to be that of lithium in graphite from [2].

Fig. 2 (a)\&(b) shows the evolution of normalized concentration \( \bar{c} \) with time for the one-way coupled and the two-way coupled systems, respectively. It is interesting to note that the steady state concentration in one-way coupled systems tend reach unity (recall that the prescribed concentration at left edge is unity) at all the six points leading to a uniform steady
state concentration in the domain. The two-way coupled system shows a very different response wherein the points E&F reach a steady state concentration greater than unity while the steady state concentration at points C&D is less than unity. At locations A&B the concentration at steady state is almost unity. It can be inferred that the local state of stress at the points in the case of two-way coupling plays a critical role in determining the maximum concentration reached. The effect of shape of the discontinuity also plays a critical role in the concentration distribution (results not shown). The above study establishes the need for considering two-way coupling in modelling stress-induced diffusion in systems such as hydrogen diffusion in metals and lithium diffusion in battery materials.

Figure 1: Schematic of the boundary value problem
Figure 2: Evolution of normalized concentration as a function of time for a plate with circular holes \((a/b = 1)\) at different locations (c.f. Fig. 1). (a) one-way coupling (b) two-way coupling.

References


Modeling electrode structures of lithium-ion batteries using the Discrete-Element-Method

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The performance of lithium-ion batteries (LIB) is strongly influenced by the composition and fabrication of the electrode structures. On the one hand, the used material and its microstructure plays an important role. On the other hand, the mechanical densification processes, such as calendering or sintering, impact on the quality of the battery. Modeling electrode structures, as it was proposed in [4], can be done in the following steps. First, the Random-Close-Packing algorithm (RCP) [3] delivers random, densely packed and overlap free assemblies of binary sized, spherical shapes, which may consist of different phases. Second, the Discrete-Element-Method (DEM) [1] is used for both densification of the assemblies by imposing uniaxial compression load as well as monitoring the intercalation induced stresses inside the structure. Densification can alternatively be modeled by so-called numerical sintering. Third, percolated clusters, which form pathways through the electrode, can now be identified by a modified Hoshen-Kopelman (HK) [2] algorithm. Finally, the structure can be represented via a Resistor-Network (RN) and – by solving the resulting system of linear equations - an effective conductivity can be calculated to evaluate the performance of the given electrode structure.

Keywords: Granular electrode structures, Effective conductivity, Percolation

References

Tuning the band gap and polarization in BaSnO$_3$/SrSnO$_3$ superlattices for photovoltaic applications

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The capture and conversion of solar energy is one of the most promising approaches to generate renewable energy due to its abundance, accessibility, and sustainability. There are two key factors that determine the efficiency of photovoltaic (PV) devices, namely, the light absorption and subsequent charge separation. A suitable band gap guarantees the ability of harvesting sunlight in the visible spectrum. The desirable separation of photo-excited carriers will promote the collection of electrons and holes and thus enhance the PV effect in the materials. Seeking PV materials with low cost and high efficiency of energy conversion is of great interest and has been subjected to intensive research explorations.

BaSnO$_3$ (BSO), a member of the alkaline-earth stannates, is a semiconducting perovskite oxide with large optical band gap and good stability at high temperature, which is a very promising material for dye-sensitized solar cells. BSO layer-based perovskite solar cells (PSCs) show better performance and have several advantages over conventional ones: (i) higher electron mobility than the widely investigated TiO$_2$-based PSCs; (ii) strain-sensitive electronic properties, leading to the mechanical control of band gap; (iii) in contrast to conventional p–n junction solar cell, where the electric field is only limited in a thin interfacial depletion layer, the polarization in BSO-based superlattice may induce additionally internal electric field that could extend over the whole volume.

Band gap and polarization are two important quantities for enhancing the performance of BSO-based photovoltaic materials. Based on first-principles calculations, we demonstrate that direct band gap and hybrid improper ferroelectric polarization coexist in
BaSnO$_3$/SrSnO$_3$ superlattices. Furthermore, the band gap and polarization can be simultaneously tuned by mechanical strain and pressure. In the presence of tensile strain or negative pressure, the band gap is substantially lowered and the polarization is enhanced by about five times in comparison with those without mechanical loads. The lowered band gap is necessary for increasing the efficiency of light absorption, whereas the enhanced polarization is desirable for the separation of photo-excited carriers in the materials. The present work suggests that the strained BaSnO$_3$/SrSnO$_3$ superlattices are promising ferroelectric semiconducting materials for photovoltaic application.

**Keywords:** photovoltaic materials, ferroelectric polarization, band gap, strain engineering.
Focused Ion Beam Reduced Graphene Oxide Micro-Supercapacitors with Unprecedented Energy and Power Densities

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Miniaturization of energy storage devices with high energy and power densities can reduce the footprint of micro-devices being used in our daily life. Micro-supercapacitors with planar geometries offer several advantages, such as, the ability to control and reduce the distances ions travel between two electrodes, easy integration to micro devices as the separator and the electrodes are in the same plane, and offer the potential of being extended into 3D without compromising the inter-electrode separation distances. In this study, we have used focused ion beam technology (which is capable of producing reduced graphene oxide patterns and complex shapes in insulating films of graphene oxide with a possible spatial resolution down to ~20 nm in a mask-less and direct write approach) to directly write miniaturized planar electrodes of reduced graphene oxide on films of graphene oxide (GO). We have optimised the ion-beam irradiation and have investigated the influence of ion beam irradiation on the resultant microstructure and the electrochemical properties of the resultant reduced graphene oxide films. Subsequently, using the optimized ion-beam irradiation, interdigitated electrode designs (40 µm long and 3.5 µm wide fingers with ultra-small inter-electrode spacing of 1 µm) have been generated, which have demonstrated a large capacitance (102 mF/cm²), ultra-small time response (0.03 ms), low equivalent series resistance (0.35 mΩ cm²), and have retained 95 % of the specific capacitance after 1000 cycles at an ultrahigh current density of 45 mA/cm². These performance metrics show unprecedented improvements on several aspects of supercapacitor performance over existing reports due to the miniaturized electrode dimensions and minimal damage to the graphene sheets. We believe our results can provide opportunities for large-scale fabrication of arrayed, planar, high performance micro-supercapacitors with a small environmental footprint.
Silicon-doped hafnium oxide antiferroelectric thin film: A promising dielectric candidate for ultracompact energy storage capacitors

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Nowadays various portable, wearable, and even implantable electronic devices have been integrated into our daily lives. There has been always a strong drive to develop these ultracompact devices as miniaturized energy autonomous systems (MEAS), consisting of signal sensing and processing units, efficient energy harvesters, and energy-storage elements. In contrast to other energy-storage methods, electrostatic capacitors are very attractive in powering MEAS as they are characterized by high-power density due to extremely high charging/discharging speed, long life and high endurance, robust thermal and mechanical stability, and parallel manufacturing capability. Two essential ingredients for an energy-storage element to succeed in ultracompact electronic devices are reduction of the footprint area and increase of the energy density. In the past years, substantial efforts have been dedicated to pack the metal-insulator-metal (MIM) trilayer capacitor in 3-dementional nanostructures, whereby the capacitance per unit planar area and the resulting energy storage can be increased significantly. Atomic layer deposition (ALD) is the only deposition technique of choice to ensure conformal and uniform growth of the metal and dielectric films. Al2O3 is the main dielectric material being used now; however, its low energy storage density (ESD) has become a constraint for practical application of electrostatic capacitors in powering microsystems. In this work, we show that this constraint can be tackled by
replacing Al₂O₃ by silicon-doped hafnium oxide antiferroelectric thin films (AFE Si:HfO₂). TiN (10 nm)/Si:HfO₂ (10 nm)/TiN (10 nm) planar capacitors were grown onto silicon substrates using ALD method. Measured at 4.5 MV/cm, very high ESD and efficiency values of 61 J/cm³ and 65% were obtained, respectively. Moreover, the energy storage performance exhibited quite robust stability in a wide temperature range (200-400 K) and even after 10⁹ times of high field cycling.

**Figure 1.** Polarization hysteresis loops of 10 nm thick Si:HfO₂ anti-ferroelectric thin film measured at different electric fields (left). Variation of energy store density, loss, and efficiency with electric field (right).
Development of an energy efficient granular phase change composite containing graphene nanoplatelets

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Abstract—This study develops a novel composite phase change material (PCM) based on paraffin/hydrophobic expanded perlite and exfoliated graphene nanoplatelets as heat transfer promoter. The experimental analysis was systematically carried out on fabrication, characterization and testing the thermal storage properties of composite PCM. The micro-morphology characteristics of composite PCM showed that the xGnP forms an interconnecting network with the porous EP, indicating the improvement in the heat transfer performance of composite PCM. Contact angle measurements showed that the composite PCM can prevent the PCM leakage in the TES system due to the hydrophobic surface properties of supporting material. Furthermore, thermal conductivity measurements revealed that the composite PCM with 1 wt% of xGnP boosts the thermal conductivity by up to 49% compared to the ordinary composite PCM.

Keywords: Phase change materials (PCMs), thermal energy storage, leakage, heat transfer performance

I. INTRODUCTION

The increased building energy consumption coupled with the depletion of fossil fuel deposits and environmental issues have promoted energy efficient building design and renewable energy systems [1]. One of the promising applications in this regard is to enhance the thermal energy storage of building envelope with the use of phase change materials (PCMs). Building elements incorporated with PCMs are meant to increase the thermal storage of the building which in turn reduces the space conditioning energy consumption and improves the indoor thermal comfort [2]. This is due to the obvious merits of PCMs such as high volumetric heat capacity and small temperature/volume variation during the thermal energy storage process. However, the barriers that are preventing wide application of PCMs in building industry are stability of PCM and heat storage performance. More precisely, the phase change behaviour of PCM covers the liquid and solid state during the operational stage which could cause the leakage of PCM from constructive system when it is liquid [3]. Furthermore, the energy storage efficiency of PCMs are limited by the low thermal conductivity of functional PCMs [4]. In this study, we fabricate a novel PCM composite based on paraffin as functional PCM and hydrophobic expanded perlite (EP) as supporting material, which prevents the leakage of liquid PCM due to the hydrophobic surface properties of supporting material. In addition, the energy storage performance of such composite PCMs were enhanced with the application of exfoliated graphene nanoplatelets (xGnP®) as the high conductive additives.
II. METHODOLOGY

A. Fabrication of paraffin/EP/xGnP composite PCM

The paraffin/EP/xGnP composite PCM was fabricated by vacuum impregnation method, where composition of materials is designed as 49.5% paraffin, 49.5% EP and 1% xGnP. The fabrication process of composite PCM is as follows. First, xGnP was dispersed in acetone by using an ultrasonic probe-sonicator. After the sonication for 30 minutes, EP was added and then xGnP/EP/acetone mix was undergone vigorous stirring for 2 hours using a magnetic stirrer equipment. After the uniform mixing of xGnP/EP, dry mixture was obtained by over-drying process. The dry mixture of xGnP/EP was then mixed with paraffin at an ambient temperature of 60°C and vacuum pressure to impregnate paraffin into the pores of EP. Finally, paraffin/EP/xGnP composite PCM was obtained after cooling down to room temperature.

B. Tests on fabricated composite PCM

The experimental works were systematically carried out to study the energy storage performance of this novel composite PCM. Micro-morphology characteristics of composite PCMs were observed using a scanning electron microscopy (SEM). The stability of composite PCM or leakage prevention in thermal energy storage system was evaluated by measuring the surface properties of composite PCM such as contact angle and wetting tension with water. Thermal performance enhancement with the addition of xGnP additives was determined by measuring the thermal conductivity of composite PCMs.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the SEM images of undispersed xGnP, EP/xGnP, paraffin/EP and paraffin/EP/xGnP mixture. Fig. 1(a) shows the undispersed xGnP before ultrasonic dispersion treatment. Fig. 1(b) shows EP/xGnP dry powder before fabricating composite PCM, where xGnP particles are connecting the inter-porous network of EP. Such high conductive connecting networks are expected to improve the heat transfer performance of paraffin. In addition, as shown in Fig. 1(d), well dispersed xGnP particles are found to be partially submerged into the paraffin of composite PCM (in comparison with Fig. 1(c)), resulting in the enhancement of thermal conductivity of pure paraffin, as expected.

The phenomenon behind the instability of composite PCMs in the thermal energy storage cementitious composites can be correlated with the contact angle and wetting tension properties between composite PCMs and water. Fig. 2 shows the contact angle measurements of composite PCMs to water. From Fig. 2, it can be seen that the hydrophobic composite PCM has negative wetting tension and contact angle larger than 90° between composite PCM and water. This indicates that the composite PCM has counter water affinity properties and thus repels the water in the cementitious composites. Due to this repellent properties, hydrophobic composite PCMs can successfully prevent the PCM leakage in cementitious composites.
The thermal enhancement with the addition of xGnP, as measured by thermal conductivity is depicted in Fig. 3. It can be clearly seen from figure that in comparison with paraffin/EP composite PCM, addition of xGnP significantly boosted the thermal conductivity with the increase level as high as 49%. This increment is expected to eliminate the poor heat transfer performance of composite PCMs in light of the application in solar energy storage and building energy conservation.

IV. CONCLUSION

In this study, the main barriers to the effective application of phase change materials (PCMs) integrated thermal energy storage cementitious composites were identified and rectified by developing a novel thermal energy storage composite. The composite PCM consists of paraffin as functional PCM and hydrophobic expanded perlite (EP) as supporting material. The poor heat transfer performance in the composite PCM was eliminated by adding 1 wt% of graphene nanoplatelets. The experimental analysis showed that this novel composite PCM can prevent the PCM leakage in the thermal energy storage system due to the hydrophobic surface properties of EP. Furthermore, integration of xGnP into the composite PCM formed an interconnecting network, which boosted the thermal conductivity of composite PCM by up to 49% compared to ordinary composite PCM.

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Parametric amplification methods for broadband vibration based energy harvesting

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With rising demands for energy, a promising future technology are vibration based energy harvester (VBEHs), which can convert ambient vibration energy into electrical energy; this energy can be potentially used for powering small electronic equipment. An important characteristic of VBEHs are that they require the natural frequency of the core element to match the ambient vibration energy, in order to harvest energy; this leads to a significant drawback for this technology, if the ambient vibration frequency shifts, the VBEH must have a large operating bandwidth to compensate.

In this work, a series of parametrically broadband vibration based energy harvesters have been designed, tested and experimentally verified. Parametric amplification has been used to increase the operating bandwidth of the fabricated energy harvester; by introducing axial excitation, large resonance behaviour at twice the fundamental resonance frequency result in large motion amplitudes—however, a minimum parametric threshold must be overcome to activate a principle parametric resonance. Furthermore, to extend the operating bandwidth, geometric nonlinearity arising from centreline extensibility has been incorporated into the VBEH designs; geometric nonlinearity resulted from large amplitude motion of the core elements about their initial equilibrium positions, this behaviour was advantageous because it caused a spring hardening effect (frequency-response curves leaning towards the right) of spring softening (frequency-response curves leaning towards the left). Moreover, the effects of tuning, mechanical stoppers, geometric imperfection have all been investigated to further extend the operating bandwidth of the VBEH. As we shall see, incorporating parametric amplification, geometric nonlinearity, tuning and mechanical stoppers can all be used to further extend the operating bandwidth and power harvested.
Tritium Generation in Fusion Reactors: Microscale Numerical Modeling of Thermomechanics of Lithium Ceramic Pebble Beds

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Success of future deuterium-tritium (DT) fusion power reactors will hinge, in part, on the ability to attain tritium fuel self-sufficiency. In many designs to be studied in the scientific fusion device ITER (see Fig. 1) as well as pre-conceptual designs of DEMOnstration fusion reactors, tritium fuel generation will happen in packed beds of lithium ceramics. A slow-moving helium purge gas crawls through the intraporeous voids in the pebble bed volume and picks up tritium generated from the transmutation of lithium interacting with neutrons. These ceramic pebble beds must endure enormous nuclear energy depositions while satisfying energy and tritium fuel production requirements. To accomplish these feats, pebble beds must maintain ceramic temperatures within relatively-narrow prescribed operating windows while facilitating transport of high quality heat into coolants flowing through structural containers. The ceramic pebble beds themselves exist with meta-stable packing structures that will evolve from thermal transients which generate external and internal forces during long-term operation as tritium breeders. As a consequence, predictive models of ceramic breeder heat transfer are vitally important and must contend with complex transitory packing structures and the changing modes of heat transfer they present.
To provide such predictive modeling, we have been developing microscale numerical models to allow fundamental investigation of thermal transport and inter-particle contact forces in pebble beds under fusion-relevant conditions. For tracking the motions and heat transfer between individual pebbles in packed bed assemblies we have employ the thermal discrete element method. Whereas pebble interaction with slow-moving, interstitial helium purge gas has been shown to be well-modeled with a volume-averaged computational fluid dynamic (CFD) method. Volume-averaged models of helium are computationally efficient and provide an overall view of helium influence on heat transfer in solid breeder pebble beds. Largely-supported open-source code (LIGGGHTS, CFDEMCoupling, etc.) have been employed as a framework upon which code development contributions have been made for application of the CFD-DEM codes to lithium ceramic pebble beds.

In this presentation, I will review recent numerical studies performed at UCLA on the thermomechanics of fusion pebble beds as well as discuss the success and role of DEM-based modeling in our Fusion Science and Technology Center. I begin with validation efforts of the thermal transport models of our DEM and CFD-DEM code; validation is performed by means of comparison to effective thermal conductivity values of ceramic pebble beds in vacuum and in stagnant helium. I will then provide an overview of many applications of the micro-scale models toward research of tritium breeding modules (TBMs) intended for use in ITER. One important application has been to address several of the most pressing thermomechanical issues for solid breeder ceramic pebble beds: fragmentation of lithium ceramic pebbles and gap formation between pebble beds and structural materials. In ITER-like representative volumes, mass re-distribution in pebble beds due to fragmentation was shown to induce subtle changes to local packing fractions yet have the ability to result in macroscopically consequential changes to temperature distributions with volumetric heating.
as shown in Fig. 2. Lastly, I will show several examples of how DEM modeling of pebble beds can provide substantial support in the lab for experimental design and analysis of pebble beds.

Figure 2: Top) temperature distribution in a cross-section with no pebble fragmentation, bottom) increased temperature distributions due to fragmentation and stress relief.
Modelling granular systems using discrete element method with elastoplastic contact model

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Granular assemblies are observed in various technological applications like fusion breeders, Li-Ion batteries, solar-thermal energy storage, pharmaceutical industry etc. Understanding the granular behaviour is essential for robust design of components having granular sub systems. Discrete Element Method (DEM) is a numerical method to simulate and understand mechanical behaviour of the granular systems. In this paper, Discrete Element Method (DEM), based on particle-particle interactions, is used to study the mechanical behaviour of a granular assembly. The effect of elastic properties of individual particles [1,2] and their crushing characteristics [3] on the macroscopic response of the assembly has been studied extensively in the literature. Studies have used elastic contact model for pebble-pebble interactions. However, the influence of plastic deformation of individual granules and the resulting contact force on the macroscopic response of the granular assembly has not been studied extensively. In this paper, approach to modelling granular systems with pebble level plasticity is investigated using in-house DEM code (DEM_KIT). An elastoplastic contact law is used to simulated the plastic behaviour of the pebbles. For elastic behaviour, Hertizian elastic contact law has been used. The plastic behaviour is modelled using linear fit to the experimental results (Fig:1). A three-dimensional assembly (Fig:1) comprising of monosized spherical pebbles subjected to uniaxial compression with both wall and periodic conditions are studied. This helps in studying the correlation between the macroscopic and microscopic properties of the granular assemblies with plastically deformable granules.
Figure 1: (a) Load-Displacement behaviour of a single steel ball under progressive cyclic compressive loading. (b) Three-dimensional pebble assembly comprising monosized spherical pebbles used in DEM simulations.

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Study on Pebble Bed Modeling and Characteristics for Water Cooled Ceramic Breeder Blanket for CFETR

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The beryllium pebble bed and Li₂TiO₃/Be₁₂Ti mixed pebble bed are selected to realize neutron multiplication and tritium breeding in the Water-cooled ceramic breeder blanket (WCCB) of China Fusion Engineering Test Reactor (CFETR). In order to evaluate and improve the performance of WCCB, studies of the thermo-mechanics and purge gas flow characteristics of the concerned pebble beds are necessary.

In the current research, a numerical model will be constructed by using distinct element method (DEM) and computational fluid dynamics (CFD) method to analyze behavior of prototypical blanket pebble bed. The suitability and validity of the current numerical model will be evaluated by comparing with the previous experimental or numerical data. Finally, the model will be extended to the pebble bed analysis of WCCB. A series of numerical simulation work, including steady-state thermal analysis, uniaxial compression test and purge gas pressure drop simulation will be conducted to obtain basic pebble bed characteristic parameter, such as effective thermal conductivity, strain-stress relation, and pressure drop. This study will be dedicated to present the heat transfer features, macro-meso mechanical behaviors and purge gas flow characteristics of the blanket pebble bed, especially the Li₂TiO₃/Be₁₂Ti mixed pebble bed for WCCB.
Exploring materials properties and materials behaviours under external stimulation using in-situ transmission electron microscopy

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The properties of materials are determined by their structures and their structural behaviours under external stimulation, including heat, applied stress and/or electric fields. Previous investigations of structure–property relationships have normally been carried out by separate structural characterisation and property measurements, which in many cases, failed to reveal the true nature of the structure–property relationships and the origins of materials properties. With recent developments in transmission electron microscopy (TEM) technology, specifically designed in-situ TEM stages are now available for the investigation of materials behaviours under various external stimuli. These TEM stages have the capability of simultaneous in-situ physical and/or mechanical property measurement and TEM imaging. Such capabilities enable researchers to correlate the measured physical, chemical and mechanical properties with the local micro- and nano-structure and structural evolution of a stimulated sample area. This is critical for revealing the structure–property relationships of materials and material behaviours under external stimuli at nanometre and/or sub-nanometre resolutions. Further, these specialised TEM stages also provide a platform for visualising and manipulating individual nanomaterials, such as nanowires and nanoparticles, and characterising their properties, which is otherwise impossible using conventional property measurement techniques used for materials with larger dimensions. In my research group in the University of Sydney, we have been using in-situ straining and biasing TEM techniques to explore extensively the mechanical properties of semiconductor nanowires and the ferroelectric properties of a few ferroelectric materials. In this presentation, I will discuss some of our recent research outcomes and will explore potential collaboration opportunities with colleagues working on energy materials.
Electrical transport in granular energy materials

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Abstract: In energy systems, granular materials are commonly used to store, convert, capture, and produce energy under complex conditions. These conditions often involve high stresses, elevated temperatures, and fast cyclic electrical charges and discharges accompanied by thermal expansion and swelling of materials. Granular systems are employed to optimize functionality and reduce risks in applications including lithium-ion batteries, fusion reactors, 3D metal printing, and flexible sensing technologies. These systems comprise assemblies of large numbers of conductive and/or insulating grains in contact. Hence, their electrical properties can be described by complex networks of randomly positioned resistors, capacitors, and inductors. These electrical networks have been observed to exhibit intrinsic electrical characteristics that show power law behaviour with respect to the frequency of the electrical signal applied. To examine these scaling laws, we present an experimental investigation of the stress-dependent electrical properties of randomly packed spheres of stainless steel, subjected to various conditions of compressive force. We considered different types of spheres exhibiting different dimensions, in order to have different inter-particle forces, which govern interfacial electrical properties, at a given stress. The frequency-dependent conductance and impedance of packed beds are found to demonstrate power-law relationships within a certain range of frequency. The absolute value of the exponent of the observed power function has been found to be independent of applied stress. The capacitive-to-inductive phase transition was observed as load increased, and was found to depend on the applied stress level and surface-to-volume ratio. The approach of equivalent network circuit was developed to describe the variation of macroscopic impedance at various frequencies. This study provides an insight into the characteristic electrical behaviours of conductive granular materials.
An insight into the thermal response of a field scale energy pile and thermally induced soil moisture migration

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Geothermal energy piles are foundation piles that utilise the almost constant temperature of the ground at given depths for space heating/cooling via a ground source heat pump. The temperature changes of the piles affect the thermo-mechanical behaviour of the pile as well as the surrounding soil properties. This paper presents the thermo-mechanical behaviour of a field scale energy pile for continuous and intermittent operating modes with natural ground recovery. The field operating conditions are physically simulated at a lab scale to study the effect of variable pile thermal loading on the soil moisture. The results presented herein are combined from studies done by Faizal et al. [1] and Cameron et al. [2]. Figures 1a and 1b shows the temperature and thermal strains in the field scale energy pile, respectively, for continuous cooling operation. Figure 2a and 2b shows the changes in soil temperature and moisture content for a model energy pile, respectively, for continuous cooling operation. The other operating modes studied are 8 hours cooling with 16 hours natural ground recovery; and 16 hours cooling with 8 hours natural ground recovery.

References


Figure 1. Results from field scale tests a) pile temperature b) thermal strains.

Figure 2. Lab scale results a) soil temperature b) soil moisture.
Experimental measurement of thermal conductivity of unsaturated porous media

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Thermal conductivity of unsaturated porous media is an important property for understanding the behaviour of soil in a number of geotechnical engineering applications such as nuclear waste repositories, brine ponds on coal seam gas sites, and geothermal energy piles. Generally, these barriers and structures are exposed to thermal gradients and operate under unsaturated conditions [1]. Therefore, a fully coupled thermo-hydro-mechanical theory for unsaturated porous media is required to describe their complex behavior. Thermal conductivity is one of the key properties that controls the distribution of the thermal gradients and consequently moisture migration through soil. Thermal conductivity of soil may change as a result of change in moisture content. A number of constitutive equations have been proposed to describe the variation in thermal conductivity from dry to saturated condition such as arithmetic, geometric, and harmonic functions (e.g see [2]).

In this study, thermal conductivity of a well graded sand as a base material for a composite lining system is measured under different degrees of saturation using a Hot Disk AB sensor (Kapton sensor). The Hot Disk method has been used for measurement of thermal conductivity of different materials [3]; however, we present a relatively simple setup consisting of two rings and two loading blocks to perform the tests (Figure 1a). A linear correlation is observed between thermal conductivity of soil and degree of saturation. Figure 1b suggests dry thermal conductivity, \( \lambda_{\text{dry}} \), and saturated thermal conductivity, \( \lambda_{\text{sat}} \), of 0.363 and 3.173, respectively.
Figure 2. Thermal conductivity measurement: a) test setup; b) results

References


GSH: from Hypoplasticity to Quasi-Elastic Behavior

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GSH (or Granular Solid Hydrodynamics) is a continuum mechanical theory constructed to account for a wide range of granular phenomena. It reduces, respectively for high and low shear rates, to the $\mu(I)$-rheology and hypoplasticity. And it uses nonlinear elasticity to account for the propagation of elastic waves, and to calculate realistic static stress distributions. An interesting question is, how does the transition between the two take place - from elasto-plastic behavior with strong plasticity to a quasi-elastic behavior with vanishing plasticity. There must be a transition, because according to hypoplasticity, elastic waves are always overdamped, and because both regimes are rate-independent. To be able to account for it, GSH needs input from good experiments executed at shear rates below $10^5$ s, or for $I \leq 10^{-8}$. 

Evaporation limited capillary penetration in porous media

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Summary Radial capillary penetration of fluids in thin porous layers is of fundamental interest in nature and various industrial applications. In practice, volatile liquid evaporates at the surface of porous media during penetration, which restricts the extent of liquid penetration to a limited region. Based on Darcy’s law and the principle of mass conservation, a general theoretical model is developed for the evaporation-limited radial capillary penetration in porous media. The model predicts that evaporation decreases the rate of fluid penetration and limits it to a critical radius. Furthermore, a unified phase diagram was constructed to describe the limited penetration of an annular porous medium.

INTRODUCTION

Capillary penetration of fluid in porous media is an important phenomenon in a broad range of applications including microfluidic devices [1], oil recovery [2], and microbial fuel cells [3], sharing a similar dynamic mechanism with capillary flow in hollow tubes. Such behaviours were described by Lucas and Washburn a century ago [4, 5]. The diffusion correlation between capillary penetration distance and time in porous media has also been found to follow the Lucas-Washburn law for both unidirectional and radial penetrations [6]. In practical applications, volatile liquid evaporates from the surface of porous media during penetration and, as a result of this continuous evaporation, the advance rate of liquid fronts is considerably diminished. Thus, the evaporation effect will induce a limited penetration process whereby liquid penetration is restricted to a limited region.

In order to quantitatively investigate the evaporation effect in unidirectional capillary penetration, Fries et al. [7] experimentally investigated the wicking of liquids into a metallic weave. The Lucas-Washburn law was employed and enhanced to model the dynamical wicking process by incorporating the effects of evaporation and gravity. For radial fluid penetration, which is widely applied in paper-based microfluidics and pumps, and textile industries, the relationship between penetration distance and time differs to that of the unidirectional case. Based on Darcy’s law and the mass conservation, a general theoretical model for evaporation-limited radial capillary penetration in homogeneous porous media is constructed. For both outward and inward radial transport, the critical radii of the limited penetration regions are determined theoretically as a function of the evaporation rate. Moreover, the limited penetration in an annular porous medium is described by a unified phase diagram to quantitatively predict the boundaries of the liquid distribution regions.

THEORETICAL ANALYSIS

Consider the evaporation weakened radial capillary penetration, as shown in Fig. 1, the evaporation rate \( m_e \), which is the mass of evaporated liquid per area and time [kg/m²·s], is used to characterize the evaporation of liquid. Assuming \( m_e \) is constant and uniform in the penetration region, the total mass flow rate due to evaporation is \( \dot{M}_e = m_e \cdot \pi (R^2 - R_0^2) \), where \( R \) and \( R_0 \) are the radii of the wetted region and liquid reservoir, respectively. For a thin porous layer with thickness \( H \) and porosity \( \varphi \), the conservation of mass during the penetration process can be obtained as

\[
2\pi r \varphi \dot{r} = 2\pi R \varphi \dot{R} + \frac{m_e}{\rho} \cdot \pi (R^2 - r^2)
\]  

where \( r \) is the local radial position, while \( \dot{r} \) and \( \dot{R} \) are the velocities of the local position and the liquid front, respectively. Furthermore, combining the Darcy’s law for liquid flow, the
\[ P_e = \frac{\mu \varphi R}{\rho} \ln \left( \frac{R}{R_0} \right) - \frac{\varphi \mu m_e}{4 k p H} \left( R^2 - R_0^2 \right) + 2 R^2 \ln \left( \frac{R}{R_0} \right) \]  

(2)

The second term of the right hand side of the above equation refers to the viscous pressure loss \( P_m \) due to the evaporation effect and represents the resistance in the penetration process, and \( P_e \) is the capillary pressure. The capillary pressure also depends on the surface tension, \( \sigma \), the contact angle formed between solid and liquid, \( \theta_s \), and the effective pore radius of the porous medium, \( R_{eff} \), with the form \( P_e = 2 \alpha \cos \theta_s / R_{eff} \). By solving the above Eq. (5), the penetration process can be predicted for both outward (\( R > R_0 \)) and inward (\( R < R_0 \)) cases theoretically. We can also find that the speed of liquid penetration reduces to zero when the capillary pressure equals to the evaporation-induced viscous pressure loss (i.e., \( P_e = P_m \)). Thus, the critical radius \( R_c \) depends on the evaporation rate, and can be obtained as

\[ (R_c / R_0)^2 [1 - 2 \ln (R_c / R_0)] = 1 - m_e^c / m_e \]

(3)

where \( m_e^c \) is a critical evaporation rate that allows inward penetrating liquid to reach the centre of the circular porous plate.

**Figure 1.** Schematic of radial capillary penetration incorporating evaporation.

**Figure 2.** Normalized radii versus time for outward penetration under different \( m_e \).

**Figure 3.** Phase diagram of evaporation limited penetration.

RESULTS AND DISCUSSION

We first consider the evaporation effect on the radial capillary penetration in a thin porous layer. According to the developed model of Eq. (5), the normalized penetration radius of the thin porous layer can be plotted versus the normalized penetration time for inward radial penetration (shown in Fig 2 for different evaporation rates). It can be seen that there exists a critical state between the limited and unlimited penetration under the condition of \( m_e = m_e^c \), which is fundamentally different from the outward case. Limited penetration occurs for an evaporation rate greater than the critical value, i.e., \( m_e > m_e^c \), and the critical radius is larger for larger evaporation rates. When \( m_e \leq m_e^c \), liquid penetrates into the whole region, but the speed of penetration still depends on the evaporation rate. From these two cases we find that the evaporation of liquid has significant effect on the radial capillary penetration.

In some practical applications of paper-based microfluidics or pumps, annular devices utilise outward and inward liquid penetrations simultaneously. Based on the above analysis, the limited penetration in an annular porous medium can be determined by two dimensionless parameters (i.e., the normalized radius of the annular, \( R / R_i \), and the normalized evaporation rate, \( m_e^c / m_e \)). Therefore, it can be described by a unified phase diagram, as shown in Fig. 3. It can be seen that the whole space is divided into three regions separated by phase boundaries (solid lines). The shaded blue and green regions describe those penetrated by the inner and outer liquid, respectively. It is interesting to see the abscissa is a constant, which means that the intersection boundary is not dependent on the evaporation rate. When the evaporation rate is larger than the critical value \( m_e^c \), there will be a dry region, as shown in yellow in Fig. 3. On the basis of this unified phase diagram, we can control the liquid penetration process or design the porous structure quantitatively.

CONCLUDING REMARKS

In this work, based on Darcy’s law and the principle of mass conservation, a general framework has been developed to quantitatively describe the evaporation effect on radial capillary penetration. The proposed model shows that evaporation has significant effects on radial capillary penetration in thin porous layers.
For both outward and inward radial capillary penetration, evaporation reduces the rate of liquid penetration. Furthermore, liquid penetration may be restricted to a limited region with a critical radius, which depends on the evaporation rate and the geometric parameters of the porous samples. For penetration in an annular porous medium, the obtained unified phase diagram shows that the outer liquid intersects with the inner liquid when the evaporation rate is smaller than a critical value. Otherwise, a dry region exists between the outer and inner liquid penetrated regions.

This study provides a quantitative theoretical exploration of the evaporation-limited radial penetration in thin layer porous media. The present analysis provides a useful framework to investigate the underlying mechanisms of limited capillary penetration in environments with non-negligible evaporation, and also warrants new designs of porous architectures to optimize the capillary penetration processes for a wide range of practical applications.

References

Thermal and energy performance of a water wall for building application

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Energy consumption by residential and commercial buildings accounts for a significant portion of the total worldwide consumption of delivered energy. Most of the energy consumption in buildings is to maintain thermal comfort through heating, ventilation and air-conditioning. It is very desirable to reduce the energy consumption in buildings, and many passive technologies have been developed for this purpose. Among them, water wall may provide a solution for certain climates. Due to the relatively large thermal mass of water, a water wall may act as a buffer zone between indoor and outdoor environments, reducing the need for heating in winter or cooling in summer.

In our study, the thermal and energy performance of a water wall system is assessed for the Sydney climate and compared with the performance of a conventional concrete wall system. Two scaled building models with a water wall and a concrete wall on the north-facing side respectively are constructed to test their performances under real climate conditions. Transient heat balance models based on energy conservation are developed for predicting the thermal performance of the water and concrete wall systems. Further, Computational Fluid Dynamics (CFD) simulations are carried out to compare the performance of the two systems under typical winter and summer climate conditions in Sydney, Australia.

It is found that over-heating of the room air may occur in the case of water wall with maximum transmissivity. The over-heating may be greatly reduced when tinting is applied to the transparent panel(s). It is also found that varying the attenuation coefficient of solar radiation in water by adding food dyes into water has an insignificant impact on the water and air temperatures, whereas increasing the thickness of the water layer can reduce the fluctuations of the water temperature and the diurnal peak air temperature. An energy performance analysis based on the CFD data indicates that an opaque water wall system performs significantly better than the concrete wall system in winter, whereas both the water wall and concrete wall systems have a similar performance in terms of energy costs in summer.
DEM-based model for the investigation of complicated thermo-chemical behaviors in gas-solid systems

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Intensive heat and mass transfer between continuum fluids and discrete particulate materials is quite common in many chemical processes. To understand and improve the operation of these processes, discrete particle models are very helpful when they are combined with the flow, heat transfer and chemical reaction models [1, 2]. This talk presents our recent developments in establishing such a particle-based model, which can be used to study thermo-chemical behaviors in gas-solid systems.

The discussion will take a blast furnace (BF) as an example (Fig. 1) [3]. The BF process represents ~70% of CO2 emission of an integrated steel plant while the steel industry contributes ~30% to the total of industrial emission. In such a process, the iron-bearing materials (e.g., pellet, lump iron ore and sinter) and coke are alternatively charged into the top of a BF. As the results of the gravitational force and the consumption of raw materials, the charged solids descend and experience strong heat load, chemical reactions, and phase transformation. It is of high significance to understand the thermo-chemical behaviors for improving its energy efficiency and hence reducing CO2 emission.

The approach developed combines the computational fluid dynamics (CFD) for continuum gas phase and the discrete element method (DEM) for discrete solid phase, supported with particle scale heat and mass transfer models (Fig. 2) [3-6]. It considers different heat transfer mechanisms in detail as well as chemical reactions. The proposed model offers a useful numerical technique not only to elucidate the fundamentals governing the heat and mass transfer at a particle scale but also to obtain useful macroscopic properties.

Keywords: CFD-DEM, heat and mass transfer, gas-solid systems
Fig. 1: Blast furnace ironmaking process (left) and raw materials (right) (iron ore pellets and coke).

Fig. 2. Exchange of information between discrete and continuum phases in the CFD-DEM model.

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