

Scanning probes for new energy materials: Probing local structure and function

Nina Balke, Dawn Bonnell, David S. Ginger, and Martijn Kemerink, Guest Editors

The design and control of materials properties, often at the nanoscale, are the foundation of many new strategies for energy generation, storage, and efficiency. Scanning probe microscopy (SPM) has evolved into a very large toolbox for the characterization of properties spanning size scales from hundreds of microns to nanometers. Recent advances in SPM involve properties and size scales of precise relevance to energy-related materials, as presented in this issue. These advances are put into the general context of energy research, and the general principles are summarized.

Scanning probes and the energy challenge

Meeting the energy needs of our maturing global civilization in an economically, environmentally, and geopolitically sustainable fashion is one of the most pressing technological challenges facing humanity today. We have heard the projections so often, sometimes we risk becoming complacent. Nevertheless, global energy consumption is on track to rise over 50% by 2035.[1] Materials scientists have a critical role to play in meeting this challenge, and major research efforts are under way to develop new technologies with the potential to dramatically improve the way we transform, store, and use energy.

Scanning probe microscopy (SPM)[2,3] is going to play a critical role in the search for new energy technologies for the reason that so many nascent energy technologies are based on nanostructured materials. For instance, organic solar cells require a large internal surface area that is currently achieved with a self-assembled nanostructured bulk heterojunction,[4] and nanoscale colloids are being used to fabricate inks for printing copper indium gallium selenide[5] and copper zinc tin sulfide solar cells.[6] Quantum dots are also under intense study for use in potential solar cells,[7] and nanostructured electrodes are critical to efficient dye-sensitized solar cells.[8] Strategies for energy harvesting based on artificial photosynthesis from biological or bio-inspired materials involve nanoscale control.[9]

Nanostructured composites and superlattices are being studied as thermoelectric materials for converting waste heat to electricity,[10] and nanostructured catalysts are being developed for solar fuel generation,[11] while metal nanostructures are being studied for enhancing light harvesting in both photovoltaic and photochemical energy conversion devices.[12] On the energy storage side, nanostructured electrodes are being used to increase capacity and improve stability of both batteries[13] and super capacitors.[14] Nanostructured catalysts can be useful for the transformation of chemical products in a more energy efficient and environmentally friendly manner.[15] SPM methods are making important contributions to energy-related materials technologies because of the unique opportunities that they offer to map nanoscale functionality such as surface potential, photoconductivity, catalytic activity, dielectric function, and even ion motion. The ability to image *function* on the nanoscale is being used to elucidate structure/function relationships in nanostructured materials for energy, often on working devices, and with exceptional resolution. **Figure 1** illustrates a fraction of the wide variety of nanostructured materials currently being studied for energy applications, in which one might imagine using functional imaging to reveal local structure-function correlations.

Scanning tunneling microscopy (STM) is the oldest technique in what is nowadays the broad field of SPM. Hence, after 25 years of routine application of atomic resolution STM, it is not surprising that properties determined from variants of STM have achieved high resolution as well. It is taken for

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DOI: 10.1557/mrs.2012.141

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https://doi.org/10.1557/mrs.2012.141 Published online by Cambridge University Press

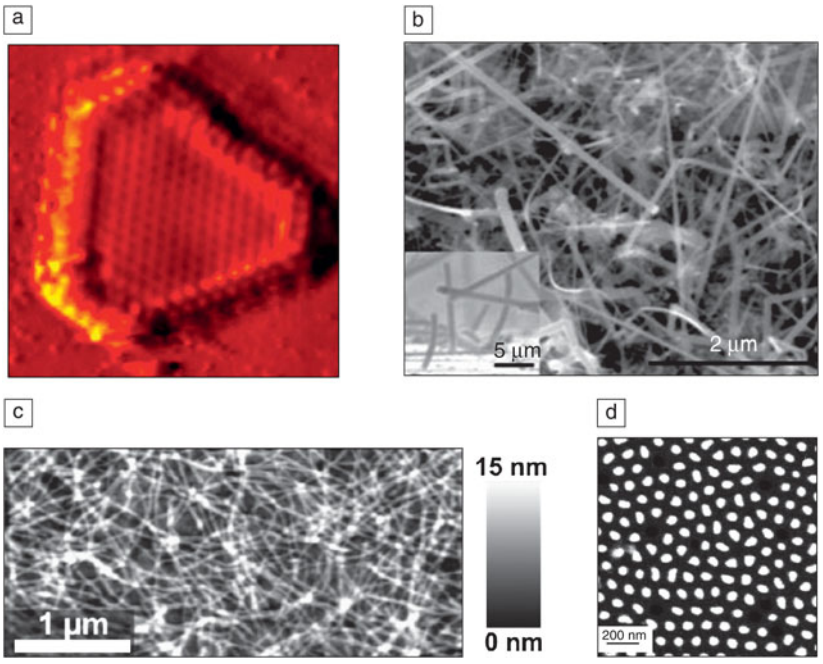


Figure 1. Examples of the range of nanostructures that are currently being studied for use in solar cells, batteries, catalysts, thermoelectrics, and a host of other energy-related materials. (a) Scanning tunneling microscopy image of a MoS_2 electrocatalyst on Au(111) (6 nm × 6 nm) (Reproduced with permission from Reference 41. ©2007, AAAS). (b) Scanning electron microscopy (SEM) image of a Si nanowire Li-ion battery anode (Reproduced with permission from Reference 42. ©2008, Nature Publishing Group). (c) Atomic force microscopy image of a nanowire organic solar cell (Reproduced with permission from Reference 43. ©2011, ACS). (d) An SEM image of electrochemically grown $Bi_2Te_{3-y}Se_y$ nanowires of potential interest for thermoelectrics (Reproduced with permission from Reference 44. ©2003, ACS).

granted that properties such as superconductor gap states and charge density waves can be mapped with atomic resolution. More surprising perhaps is the spatial resolution achieved while probing continuum properties. Resistance and capacitance can be mapped with 1–100 nanometer (nm) resolution,[16–18] while atomic and molecular resolution have been achieved for the work function and dielectric constant, respectively.[19,20]

As highlighted by the examples on the following pages, recent advances apply these abilities to make measurements of complex properties in situations of relevance to energy devices. *In situ* SPM now probes device materials in the presence of both electric field and optical excitation, measures local electrochemistry in solution, and more.[1,4] For example, catalysis does not occur in a vacuum. New high pressure systems allow catalytic interactions to be probed under realistic environmental conditions, as described in the review by Besenbacher et al. Catalysis and electrochemistry can now be characterized in liquids, as summarized by Lai et al. Similarly, many photovoltaic devices involve the interaction of light with nanostructured materials to generate charge carriers, and O'Dea et al. review the many applications of SPM to understand both organic and inorganic thin-film photovoltaics. Lee et al. exploit local impedance probes to examine interactions in oxide fuel cells, lithium-ion batteries, and light harvesting proteins.

Not just surface topography

To a newcomer, the field of SPM can sometimes seem like a confusing alphabet soup of specialized techniques. The explosion of acronyms reflects the breadth and creativity of activity in this area. The precise control of the tip-surface junction became a platform for diverse property measurements. While it would be impossible to provide a comprehensive review of scanning probes in this issue, we try to provide the general reader with a high-level overview and some insight into the common vocabulary found in the feature articles that follow. **Table I** gives a concise summary of the popular techniques, many of which are featured in this issue of *MRS Bulletin*.

The invention of STM revolutionized (nano) science and founded the field of SPM.[21] In brief, STM is based on the exponential distance dependence of the tunneling current between a conducting tip and sample. By laterally scanning the tip with respect to the sample, or vice versa, atomic resolution can be obtained in the tunneling current or in the height signal. In the former case, a feedback system is used to keep the tip-sample distance (tunneling current) constant. In scanning tunneling spectroscopy (STS), the feedback loop is briefly opened, enabling the local measurement of current-voltage characteristics.[21]

The field of SPM generalizes the approach of a tip-surface probe to an extensive range of interactions and, therefore, properties. In the following paragraphs, we give a brief introduction to scanning Kelvin probe microscopy (SKPM)[22] (also called Kelvin probe force microscopy [KPFM]) and electrostatic force microscopy (EFM),[23,24] see also **Figure 2**. These techniques are two of the main workhorses for the local probing of functional properties and are intensively used for energy materials (see also the O'Dea et al. article). The more interested reader is referred to the extensive literature on this topic (e.g., Reference 25). The principle of SKPM and EFM is not unlike that of topographic atomic force microscopy (AFM) in the sense that an interaction force between the surface of interest and the apex of a sharp tip is probed in some way. The major difference is that AFM probes the surface topography via short range, Lennard-Jones-type potentials, whereas EFM and SKPM probe the surface potential via the Coulomb interaction.

Due to the long-range nature of the Coulomb force, truly "local" measurements in SKPM and EFM are challenging; nevertheless, atomic resolution has been obtained with SKPM, although this is the subject of some controversy.[26,27] Like in AFM, EFM and SKPM signals can be extracted from either the interaction force itself or from the force gradient. Although these signals could, in principle, be probed in dc mode (cf. contact mode AFM), EFM and SKPM are always performed in ac (non-contact) mode, in which the tip oscillates

https://doi.org/10.1557/mrs.2012.141 Published online by Cambridge University Press

Table I. Overview of scanning probe microscopy-based techniques for probing functional properties.

	Force-Based		Electronic Current-Based		Ionic Current-Based	Electromagnetic Fields
	Contact	Non-contact (nc)	dc Current	ac Current		
Detection Principle	Mechanical forces	Electrostatic fields	Electronic current	Impedance	Ionic current	Optical and electromagnetic fields
Methods	AFM, EC-AFM, ESM, PFM	nc-AFM, EFM, KPFM, SIM	STM, EC-STM, C-AFM, pc-AFM	NIM	SICM, SECM, SMCM, SECCM	NSOM, μ-Raman, SMM
Probed Information	Topography, electrochemical and piezoelectric strain	Topography, surface potential, work-function, capacitance	Tip-surface current	Impedance, dielectric function	Electrochemical current and voltage	Absorption, emission, light field intensity, vibronic properties
Lateral Resolution (best case)	1–10 nm	1–10 nm	0.1–10 nm	20 nm	0.5–500 nm	50 nm

AFM, Atomic force microscopy; EC-AFM, electrochemical atomic force microscopy; ESM, electrochemical strain microscopy; PFM, piezo force microscopy; EFM, electrostatic force microscopy; KPFM, Kelvin probe force microscopy; SIM, scanning impedance microscopy; STM, scanning tunneling microscopy; EC-STM, electrochemical scanning tunneling microscopy; C-AFM, conductive atomic force microscopy; pc-AFM, photoconductive atomic force microscopy; NIM, nanoimpedance microscopy; SICM, scanning ion-conductance microscopy; SECM, scanning electrochemical microscopy; SMCM, scanning micropipette contact method; SECCM, scanning electrochemical cell microscopy; NSOM, near-field scanning optical microscopy; SMM, near-field scanning microwave microscopy.

with respect to the sample, as this gives a superior signal-to-noise ratio. For both techniques, an ac bias with frequency ω is applied to the tip or sample. Treating the tip as a simple harmonic oscillator, it is easy to derive that the Coulomb force between the tip and sample is proportional to dC/dz, with C being the tip-sample capacitance and z the tip-sample distance, and gives rise to tip oscillations at ω and 2ω. Similarly, the force gradient is proportional to d^2C/dz^2 and causes an oscillating shift of the tip's resonance frequency.[25] Since capacitance scales in the lowest order as $C \propto 1/z$, it follows that force gradient detection is least susceptible to (undesired) couplings between the sample and parts of the tip other than its apex. Hence, force gradient detection typically shows superior spatial resolution. By working at one of the cantilever resonances, detection is usually more sensitive.

The working principle of EFM and SKPM is explained in Figure 2. When two metals with different work functions W are connected (Figure 2a), an electric field (shown as a gradient in the vacuum level E_{vac}) is created and exerts a force (and force gradient) on the tip. In SKPM, this force is nullified by applying a compensating bias V_{SKPM} via a feedback system (Figure 2b); in EFM, this feedback is absent, and the force (gradient) itself is mapped. In the situation of Figure 2b, SKPM probes the work function difference W_{surf}–W_{tip} between the tip and the sample surface. Insertion of an ideal intrinsic semiconductor (characterized by its ionization potential IP and electron affinity EA) between the tip and sample (Figure 2c) has no effect on the SKPM signal. In the case in which an interfacial dipole layer exists between the substrate and semiconductor or when the semiconductor contains bulk uncompensated charges (Figure 2d), the SKPM signal changes: by nullifying the force on the tip, the feedback nullifies the electric field at the tip. Generally, SKPM probes the electrostatic potential of the sample and, in special cases (Figure 2b–c), statements about the sample work function or Fermi level can be made.

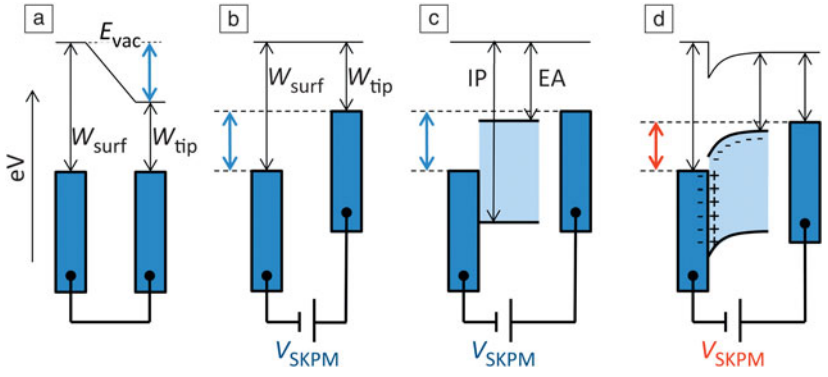


Figure 2. Illustration of electrostatic force microscopy (EFM) and scanning Kelvin probe microscopy (SKPM). Dark blue rectangles indicate the metallic tip and sample (a–b) or substrate (c–d). The light blue regions in (c) and (d) indicate a semiconductor. The electrostatic force between the tip and sample is probed in EFM (a); nullification of this force in SKPM (b) enables quantitative surface potential measurements, which may be complicated by the presence of a semiconductor (c), causing interfacial dipoles or space charges (d). E_{vac}, electric field in a vacuum; W_{surf}, work function of sample surface; W_{tip}, work function of tip; V_{SKPM}, compensating bias in SKPM; IP, ionization potential; and EA, electron affinity.

Probing more complex properties

SPM-based methods that probe dynamic material responses sometimes require multi-frequency excitation and detection. These

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methods include approaches to accessing piezoelectric and ferroelectric interactions, dielectric function, and ionic motion. Such properties are critical to several energy storage and conversion strategies.

One technique, important for piezoelectric materials used for information storage and energy harvesting, is piezoresponse force microscopy (PFM).[28] PFM probes the electromechanical material response (i.e., a change in strain in response to an electronic stimulus). Here, a single frequency ac bias, V_{ac}, is applied to a conductive SPM tip in contact with the sample surface. As a consequence of the piezoelectric effect, described by a linear relationship between the strain, *S,* and electric field, *E*, with the piezoelectric coefficient, *d,* as a proportionality constant, a change in strain is induced by the electric field. The dynamic strain change in response to the applied V_{ac} can be detected as a surface oscillation with the same tip used to apply the electric field. Using lock-in techniques, the amplitude and phase of the sample response can be extracted, and information about the local piezoelectric strength and domain orientation can be mapped. In addition to domain imaging, PFM can be used to manipulate the domain orientation by applying a dc bias, V_{dc}. Applications of domain manipulation include domain poling and measurements of local piezoelectric hysteresis. PFM has been widely used on various materials such as ceramics,[29] thin films,[30] polymers,[31,32] and biological samples[33] and has become a standard characterization technique that is commercially available.

A recent advancement of PFM is high-frequency PFM, where the contact resonance peak of the tip-sample system is utilized to achieve 100 times higher signal/noise ratios compared to off-resonance PFM. With this development came the need for multiple frequency excitation and detection because of ambiguities associated with the dependence of the contact resonance frequency on sample roughness and tip state that results in falsified information when single frequency methods are used. Currently, multiple frequency techniques are realized through dual ac resonance tracking[34] and band excitation,[35] described in the article by Jesse et al. in this issue of *MRS Bulletin.* The use of multiple frequency techniques is not limited to PFM but can be applied to other non-contact SPM techniques as well.

The concept of PFM (i.e., the characterization of electromechanical sample properties) is not exclusively used for piezoelectric materials but can be applied to every sample system where a strain change can be induced by bias. This concept led to the development of electrochemical strain microscopy (ESM) for energy storage materials, including Li-ion batteries[36,37] and solid oxide fuel cells.[38] Here, the locally applied bias changes the local ion concentration (Li^+ or O^{2-}), which results in a change in sample volume. For Li-ion battery materials, this can be up to 400% for Si anodes. With the development of ESM, it is possible to investigate the local ionic transport on relevant lengths scales of single microstructural elements down to 10 nm, which was not possible before.

Polarization is a complex property represented by the dielectric constant κ, which plays a major role in many materials in energy generation and storage systems. Dielectric polarization is inherent in the interaction of light with solids, the motion of ions in ionic materials, electrical charges trapped at interfaces, and dipoles in organic and biomolecules. Recent strategies to locally probe dielectric function involve light scattering from a tip-surface junction,[39] second harmonic capacitance gradient detection in EFM, and scanning impedance microscopy and its variants.[40] Impedance is defined as the (complex) ratio of a periodically varying applied voltage to the resulting current and is measured as a function of frequency. The combination of impedance with SPM allows the real and imaginary components of the dielectric function to be accessed with high spatial resolution. Fundamental processes such as charge trapping-relaxation, ion diffusion, and molecular dipole reorientation occur at different time scales which, in principle, can be distinguished with scanning impedance probes. In the article by Lee et al., applications in Nafion, as a proton exchange membrane for fuel cells, Li battery-based materials, and energy harvesting protein systems, are explored.

Future opportunities

The first generation of scanning probe microscopy (SPM) techniques—scanning tunneling microscopy, atomic force microscopy, and electrostatic and magnetic force microscopies—are now considered essential tools in materials characterization and are used routinely in basic and applied research as well as industry-based development. However, the potential of the second and third generation techniques may not be well known, partially due to the fact that the most advanced techniques are not yet available commercially. When they are commercially available, for example, as in the case of KPFM, they have a tremendous impact. As the articles in this issue illustrate, the solutions to our energy challenges demand the characterization of local functional properties. We hope that the reviews in this issue will inspire and enable many to exploit these tools in energy research.

From the perspective of fundamental research of SPM itself, it is an exciting time. Rather than standing on a maturity plateau after the first two decades, we are poised at the beginning of a new generation in SPM technology as we push the spatial resolution of functional probes to higher levels. These advances will in turn propel our fundamental understanding of energy-related materials and enable solutions to some of our most important energy challenges.

Acknowledgments

D.B. is grateful for support from the DoE Office of Basic Energy Science, Division of Materials Science DE-FG02-00ER45813, and the National Science Foundation NSEC DMR08-32802.

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