Atomic Force Microscopy (AFM) in Battery Research & Development

1. Introduction

Transformation of energy sources from fossil fuels to renewables is on the table and actively pursued by various stakeholders to achieve the sustainability of modern life. However, renewables like wind and sun are only available intermittently and therefore require the extracted energy stored for later use as electricity. Moreover, transportation is relying more and more on electric vehicles, which again depend on stored electrochemical energy. Hence it is indisputable that batteries will play a central role in our progress towards green energy.

Industry trends tell the same. The automotive industry shows determination to turn away from internal combustion engines. For example, General Motors have promised to sell only zero-emission vehicles by 2035.[i] Electric vehicles accounted for almost 9 percent of new car sales worldwide in 2021.[ii] Even conservative estimates predict the number will reach 18 percent by 2030, requiring batteries eight times the current production capacity.[iii]

The upward trend in electric vehicles is made possible by the declining prices of lithium-ion batteries. Prices have dropped from $1,000/kWh in 2010 to nearly $200/kWh in 2017 and are expected to be $100/kWh by 2025.[iv] Batteries are the most expensive component of electric vehicles, comprising 30% of the price of an average mid-size car.[v] For electric vehicles to be competitive and attain mass attraction, battery prices should be at least half the current prices.[iii]

Technological improvements are necessary for batteries to become cheaper. Besides lower prices, batteries should also have better durability, safety, reliability, cycle and shelf life, energy density (i.e., storage capacity), and power output to support the transformation in many facets of society. Via powering electronic gadgets, such as cell phones and laptops, Li-ion rechargeable batteries (LIB) enabled the current wireless lifestyle. Their further sophistication upon the first marketed $Li_{1-x}CoO_2/C$ cell (Fig.1) has been achieved mainly by cell engineering, which includes controlling the size and morphology of active particles and the architecture of current collectors.[vi] However, according to John B. Goodenough, who won the Nobel Prize in Chemistry for his work on lithium-ion batteries, that sort of engineering has reached its limits.[vi] For larger-scale energy storing, like electrical grids and electric vehicles require, thus they can compete with established practices, new

chemistries and alternative materials for battery components, and novel battery designs and strategies for storing energy are needed.

A better understanding of how batteries work at the nanoscale could pave the way to much-sought technologies. Batteries store energy in chemicals that can ionize readily to give up their electrons. In a LIB, Li ions move back and forth between anode and cathode - electrodes where redox reactions (i.e., Li ions take and release electrons) occur. During discharge, the anode becoming negatively charged releases Li-ions to move the cathode through a liquid electrolyte. As a result, electrons move from the negatively charged anode to the positively charged cathode via an external circuit forming an electrical current that can do a work, such as turning on a light bulb (Fig. 1). When

charging a battery, the opposite happens. Li-ions move back to the anode through electrolyte solution, while electrons are brought back from the now negatively charged cathode to the positive anode via the circuit. Theoretically, this cycle could go on indefinitely, but it fails in practice as batteries become unreliable after a certain amount of usage. And the failure starts at the nanoscale. Analysis of how failure generates and propagates could be crucial for improving current technology. Apart from failure analysis, understanding the behavior of battery materials with nanoscale precision and informing the design process shows the potential to reinvigorate the stalled battery technologies. As we are to see in this paper, nanoscale topographical, mechanical, or electrical patterns of battery parts are strongly related to the macroscopic characteristics of batteries.
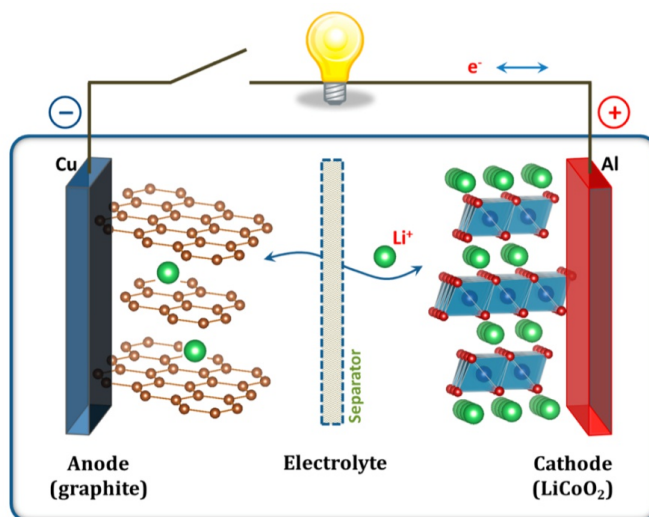

Figure 1. *Schematics of a Li-ion battery. Anode made up of graphite releases Li ions through a liquid electrolyte while becoming charged negatively with electrons given up by Li atoms. Li ions move through a membrane named a separator to reach the cathode, made up of LiCoO2. The potential difference built between the anode and cathode in the process drives electrons to move to the cathode if an external circuit exists and generates an electric current (taken from ref. 6)*

We believe that nanotechnology, a blossoming scientific and technological field, is ready to bring solutions to the problems in battery research. It can provide numerous methods and tools for material design, processing, measurement, and imaging, all at nanoscale precision, that could revolutionize lithium-ion and other kinds of batteries. Atomic Force Microscope (AFM) stands out among these tools with its unmatched characteristics regarding the imaging and analysis of surfaces. In this paper, we discuss the importance of AFM in battery research and show relevant examples from academic research.

2. Introduction to AFM

The working principle of the Atomic Force Microscope (AFM) is based on the forces that arise when a sample surface is scanned with a nanometer-sized tip (a few to 10s of nm) attached to a cantilever. The advancement of the AFM over traditional stylus surface profilers is that the former uses a feedback loop to control the forces between the surface and probe. Because the forces are controlled, very small probes may be used, and not broken while capturing an image. There are two primary modes used for measuring a sample's topography: contact mode and vibrating mode.
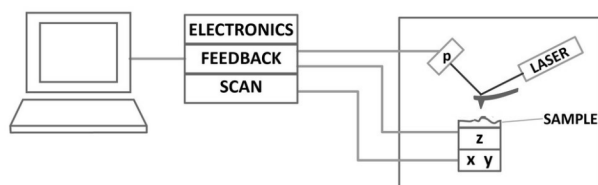
Contact mode: The probing tip is in contact with the surface throughout the imaging in contact mode. The short-range forces between the surface and tip cause the deflection of the cantilever, which is recorded to generate the topographical image of the surface. However, the tip-surface contact in this mode can potentially damage the surface or wear the tip. Hence, this mode may not be suitable for imaging of soft surfaces. On the other hand, continuous contact with the surface allows identifying other features such as friction (lateral force imaging) or stiffness/elasticity map of the surface (force modulation imaging). In lateral force or frictional force microscopy, lateral deflections of the cantilever, arising due to forces parallel to the plane of the sample surface, such as friction force, are measured.[vii] This allows detecting inhomogeneities on the material, leading to variations in surface friction.

Vibrating Mode: In this mode, a probe at the end of a cantilever is vibrated up and down. As the vibrating probe begins to interact with a surface, the vibration amplitude is dampened. The amount of damping is proportional to the force placed on the surface by the probe on each oscillation of a vibrating probe. A feedback loop is used to maintain a fixed vibration amplitude as the probe is scanned across a surface. Forces between the probe and surface in vibrating mode can be as low as a few 10's of piconewtons.
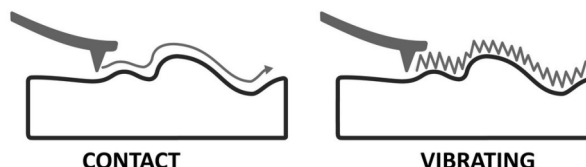
Although AFM is widely known for mapping surface topography, that alone does not

always provide the answers that researchers need to understand the material.[viii] Fortunately, as a result of its capability to measure varying forces arising between the tip and sample, AFM can characterize a wide array of mechanical properties (e.g., adhesion, stiffness, friction, dissipation, viscoelasticity), electrical properties (e.g., capacitance, electrostatic forces, work function, electrical current, conductivity, surface potential, resistance), magnetic properties, optical/spectroscopic properties, thermal properties, and solvent effects (via imaging at liquid environment) in almost real-time.[ix]

Phase imaging: A phase difference between oscillation of the cantilever and of the signal that drives cantilever oscillation (for example, piezoelectric crystal) is measured and visualized in phase imaging.[x] There is no phase contrast when the surface is homogenous, or there is no interaction between the tip and surface (i.e., the cantilever is well above the surface). However, if specific surface regions have distinct mechanical properties, phase imaging could capture that variation. That is because the cantilever loses a different amount of energy as the probe taps to surface areas with differing mechanical properties. Hence, phase imaging could help detect variations in mechanical properties such as friction, adhesion, and viscoelasticity on surfaces. It could as well be used to detect patterns of various materials such as polymers on the surface or to identify contaminants that can not be distinguished with topography imaging.

3. Relevant applications of AFM in battery research

3.1. Electrolyte development

The lithium-ion batteries in most electric cars have liquid electrolytes enabling the transfer of lithium ions between anode and cathode. However, they can be volatile and flammable at high temperatures, such as when the battery is charged-discharged quickly or damaged in accidents.[xi] Therefore, scientists search for solid alternatives to liquid electrolytes that would be safer yet lighter. Solid electrolytes also allow researchers to design these batteries as thin films, which would provide more versatility in packaging.

Currently available materials for solid electrolytes require high temperatures to achieve comparable conductivity to liquid electrolytes. However, high temperatures affect the long-term performance and durability of batteries. To solve the problem, Park et al. designed a novel nanomaterial named Yttrium-doped barium zirconate (BYZ), which possesses higher ionic conductivity at appropriate temperatures enabling it to serve as a solid electrolyte.[xii] They used the pulsed laser deposition (PLD) technique to obtain electrolytes with varying thicknesses and tested the electrochemical performance of solid oxide fuel cells that employ these electrolyte materials. Inquiring whether the roughness of the electrolyte surface is related to its performance, they utilized AFM imaging to characterize the surface topography of electrolyte nanomaterials stated above. They observed that the surface roughness of BYZ electrolytes increased linearly with their thickness (Fig. 2). It turned out that

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electrochemical performance, as measured by open circuit voltage, was higher with the thickest electrolyte. Authors concluded that higher roughness blocks pinholes in the material and increases reaction area, thereby elevating its performance.
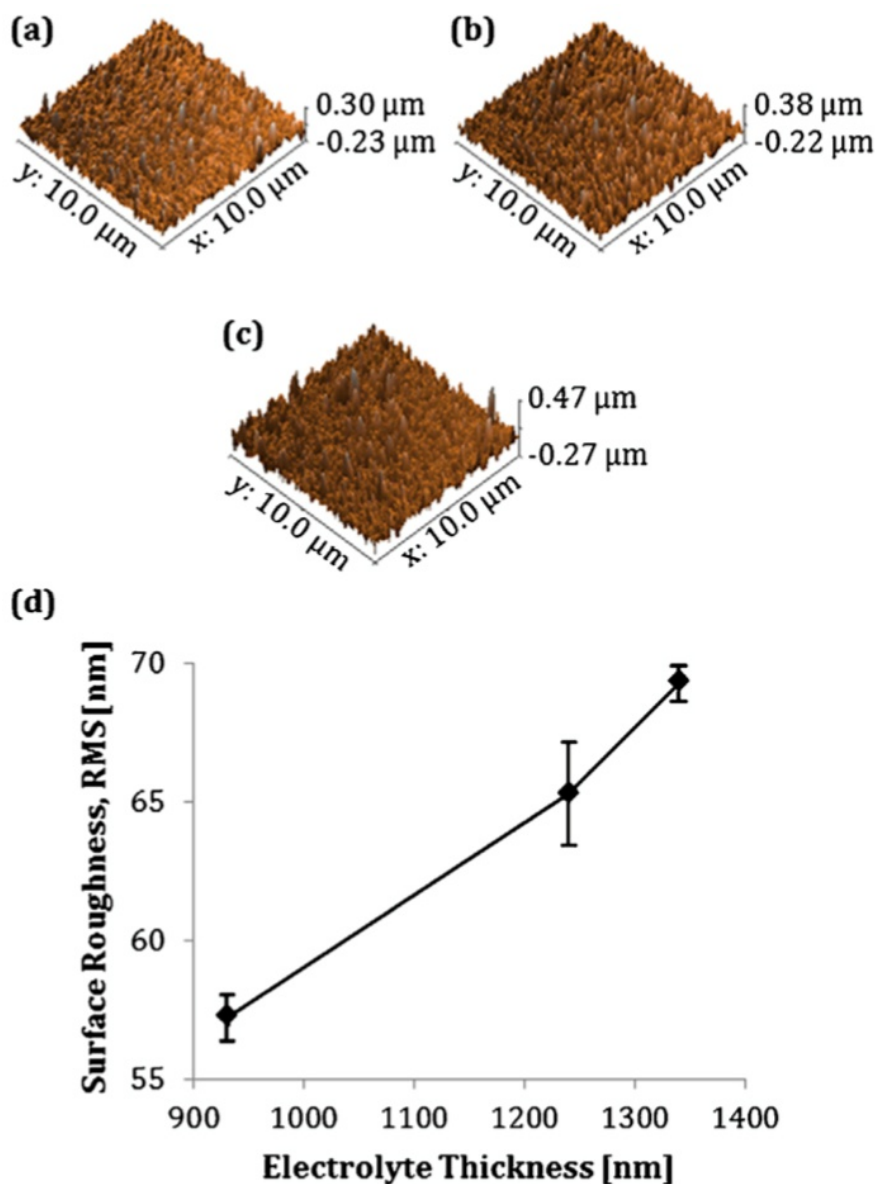

Figure 2. *AFM helped researchers to examine correlation between the thickness of the Y-doped BaZrO3 (BYZ) thin film solid electrolyte and its surface roughness. AFM images of the electrolyte surfaces with (a) 930 nm-, (b) 1240 nm-, and (c) 1340 nm thicknesses are displayed. Also shown is the graph depicting how surface roughness RMS value changes per thickness of the electrolyte (d). The surface topographies were scanned with AFMWorkshopTM AFM in contact mode (taken from ref. 12).*

3.2. Separator development

The separator membrane is a crucial part of currently marketed batteries. It separates an electrolyte into two parts: one contacting with anode and the other with the cathode. Separator materials are typically selectively permeable to charged electron carriers (e.g., Li ions in Li-ion batteries) while non-conductive to electrons, thus preventing self-discharge (though a bit of the latter still occurs). The development of new materials could help improve the capabilities of the currently available batteries while facilitating the entrance of new battery designs into the market.

Current research efforts to improve separator technology are particularly focused on batteries collectively called flow batteries or redox flow batteries. Unlike the conventional battery design, as given in Fig. 1, the flow battery design keeps electrolytes that hold electron carriers in the tanks outside the cell, where electrochemical reactions occur (Fig. 3).[xiii] Decoupling energy storage and power generation allows for designing energy storage and power output units independently and more flexibly.[xiv] This design is especially fitting for the medium to large-scale energy storage systems as it is possible to expand the size of the electrolyte tanks.
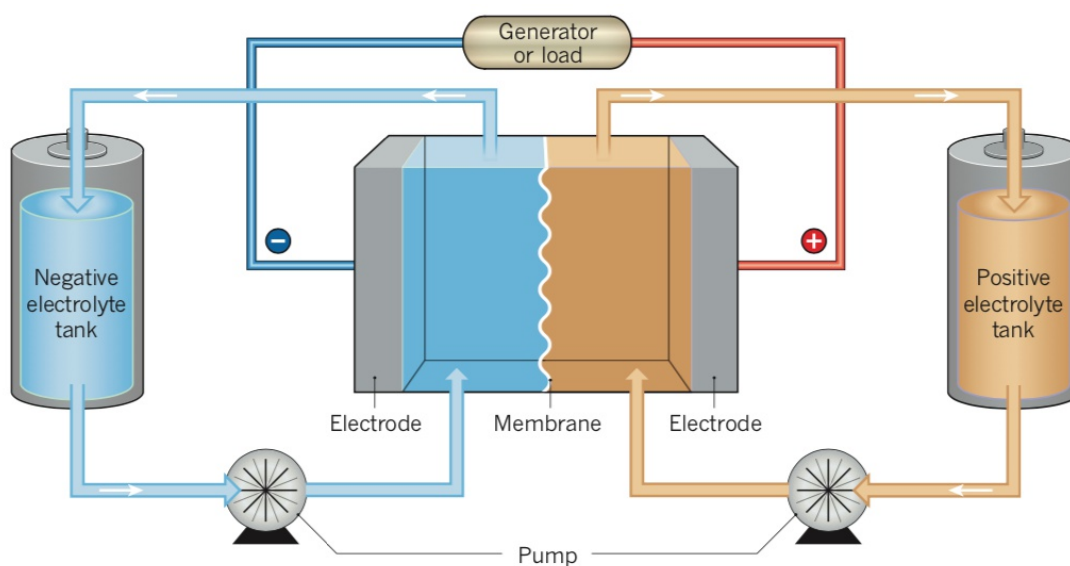

Figure 3. Redox flow batteries (RFBs) or flow batteries have their energy-storing material, such as a metal or a polymer dissolved in a liquid electrolyte throughout charge/discharge cycles. Instead of having a single electrolyte as in Li-ion batteries, RFBs have two different electrolytes, a negative electrolyte (also called anolyte) and a positive electrolyte (also called catholyte). These liquids are stored in two separate tanks and pumped through electrodes, where a separator membrane prevents their mixing. During discharge, an anolyte delivers electrons produced in a redox reaction to the negative electrode. The electrons are transferred from the negative electrode to the positive electrode via an external circuit. In a catholyte, electrons reduce relevant compounds in another redox reaction. Circulation between reaction cells and tanks continues until the battery ceases to deliver power. (taken from ref. 13).

Scientists regard lithium-sulfur battery as a promising technology because it can provide higher specific energy (i.e., energy per mass) than conventional Li-ion batteries, and sulfur (instead of cobalt in Li-ion) is an abundant raw material. Many problems associated with its scaling up seem to be alleviated using liquid Li2S8 "catholyte" instead of the solid sulfur cathode.15 However, the applicability of these lithium polysulfide (Li-PS) redox flow batteries is hindered by "the poor solubility of short PS chains in organic electrolytes and the crossover of intermediate PS species between the cathode and anode." As a result, battery capacity decreases rapidly. Wang et al. designed a nanocomposite separator material that allows the passage of Li ions while non-permeable to polysulfide species.[xv] The two-layered material,

well as the distribution of bundle and pore sizes on the surface (Fig. 4). Those parameters are critical to evaluate the quality of the material, as they limit the scope of molecules which could pass the membrane. Li+/PS− selectivity of the separator was provided by the polymer (biphenyl-based cation-exchange polymer) loaded into the carbon nanotube (CNT) layer. It was also possible to compare unloaded and loaded CNT layers based on their AFM images and verify polymer deposition and intactness of carbon nanotubes.

Redox flow batteries commonly use metal vanadium dissolved in acid as a carrier of electrons.[xiii] The nanoscale structure of the membranes used as separators in vanadium redox flow batteries (VRFB) is critical for their optimal functioning. These membranes are expected to have high proton
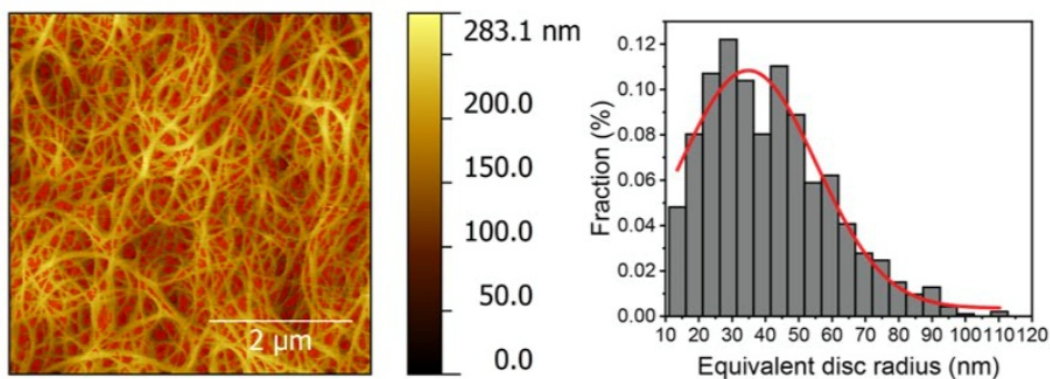
Figure 4. AFM image and pore size analysis of the carbon nanotube layer of the multifunctional electrochemical membrane. The surfaces were scanned with AFMWorkshopTM TT-AFM equipment in vibrating mode (taken from ref. 15).

composed of a carbon nanotube-based layer facing the cathode and a boron nitride nanotube layer facing the anode, was analyzed morphologically by AFM. The analysis provided the images of the material surface with nanometer-level precision, as

conductivity to reduce internal resistance, low vanadium and water permeability to prevent crossover, chemical inertness and mechanical robustness to withstand highly acidic RFB conditions, and low cost to be market competitive.[xvi] Gindt et al.

synthesized and evaluated PLA–PSU–PLA triblock copolymer nanoporous membrane of polysulfone (PSU) and polylactide (PLA) as a separator membrane. vibrating mode AFM has been used to characterize the membrane's nanoscale structure and mechanical properties. While topography imaging indicated an almost flat surface, phase imaging of the same surface revealed a phase-separated morphology and distinct domains with 20-30 nm sizes (Fig. 5). Differences in the mechanical properties of domains resulting from variations in material composition between domains are highly likely behind such phase contrasts. These

Comparing a phase image of a surface with a topographical one allows for detecting such material deterioration. This study demonstrates the richness of information one can obtain by employing various AFM techniques to investigate any surface.

3.3. Electrode materials

Battery electrodes can be considered the most central part of batteries. At one part, they transfer electrons released due to redox reactions to a current collector or accept incoming electrons from the circuit. On the
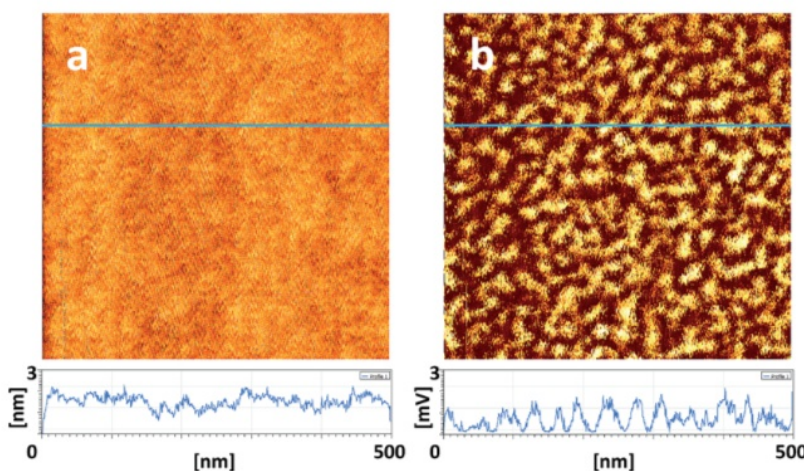
Figure 5. AFM imaging of PLA–PSU–PLA triblock copolymer membrane developed as a separator membrane for vanadium redox flow batteries. The membrane surfaces were scanned with AFMWorkshopTM TT-AFM in the vibrating mode. Pictures depict topography (a) and phase (b) images of the same surface (taken from ref. 16).

phase contrasts might be a signature of membrane functionality. Damages that alter the membrane's chemical composition and structural integrity might cause severe changes in ion channels and other substructures. While such damages affect membrane functionality seriously, they may not cause any change in topography.

other part, they are in contact with the electrolyte and either give ions to or take from it. Hence, their design needs the utmost care. Electrodes should be conductive, inert to the electrolyte, and resilient to redox reactions at each cycle. One safety problem with Li-based batteries that also thwarts the development of some battery technologies is

the formation of dendritic structures, contacting the opposite pole, and making a short circuit.[xvii] Understanding these processes could lead to groundbreaking solutions in the field. AFM, with its potential characterizing properties of electrodes, such as conductivity and morphology at the nanoscale, is poised to play an indispensable role.

The surface area of electrodes is a critical parameter in their functioning since it affects the ion transfer between electrode and electrolyte. Variations in synthesis protocols could give rise to electrode materials with different surface areas. It is also essential to understand the changes in surface areas of battery electrodes upon specific amounts of cycles to document their resilience to usage. Fortunately, AFM topography imaging identifies the peaks and valleys on the material surface at nanoscale precision, thus determining the surface area.

Caneppele et al. built porous electrodes for fuel cells by dispersing Pt/C (platinum on carbon) nanoparticles on carbon paper (Pt/C/CP electrodes).[xviii] As catalysis depends on the surface area available, they aimed to increase the latter by dispersing Pt/C nanocatalysts over carbon fiber. They employed AFM topography imaging to
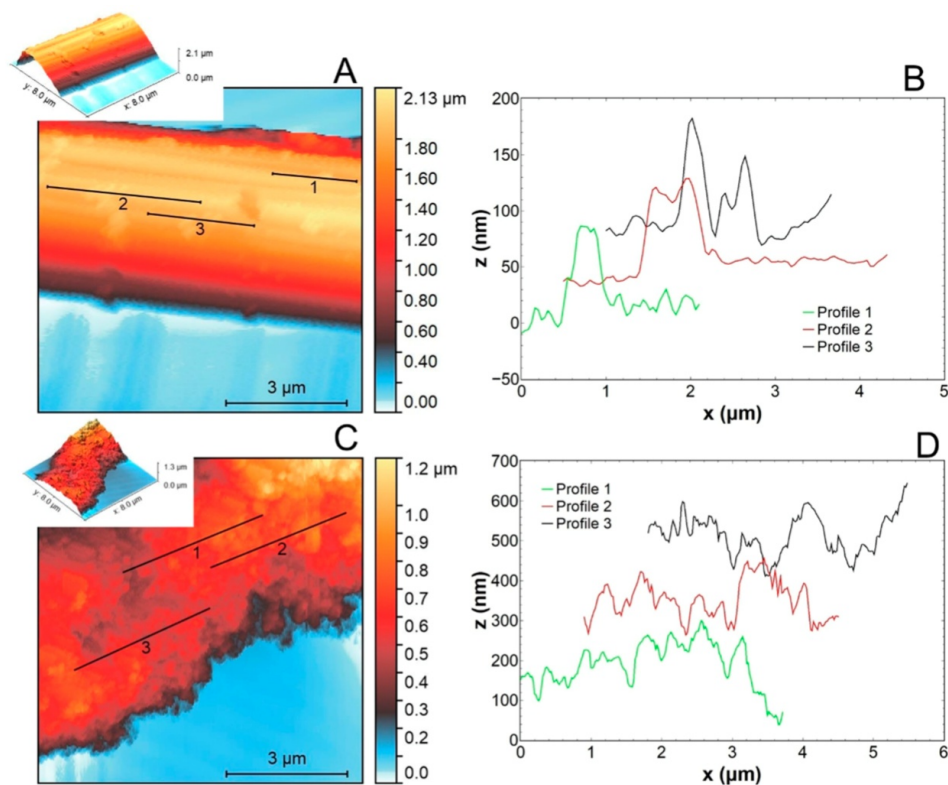
Figure 6. AFM imaging identified the topography of the electrodes obtained by dispersing Pt/C (platinum on carbon) nanoparticles on carbon paper (Pt/C/CP electrodes). The effects of two methods - immersion (a, b) and ultrasonic bath (c, d) - on dispersion profiles of nanoparticles on carbon paper were revealed by using AFMWorkshopTM TT-2 AFM in the vibrating mode. Scanning included 8.0 × 8.0 µm regions from the surfaces of both electrodes (insets: a, c). Graphs on the right indicate the topographic profiles of the images over the lines shown on the pictures (taken from ref. 18).

compare the two methods they used to prepare electrode materials (Fig. 6). They either immersed carbon paper in Pt/C ink or kept it in an ultrasonic bath with the ink. AFM imaging showed localized aggregates rather than the dispersion of Pt/C nanoparticles on carbon fibers with the immersion method (Fig. 6a). These aggregates reached ~ 90 nm in height and ~ 1 µm in diameter (Fig. 6b). There was also a sizeable metal-free region on the fiber. On the other hand, electrodes prepared with the ultrasonic bath method showed extensive coverage by nanocatalysts with height changing around ~ 90 nm (Fig. 6c, d). In addition, the latter electrode in glucose electrooxidation generated ~2.5 times more current density than the electrode produced by the immersion method. The authors explained this enhanced activity by increasing surface area with the ultrasonic bath method.
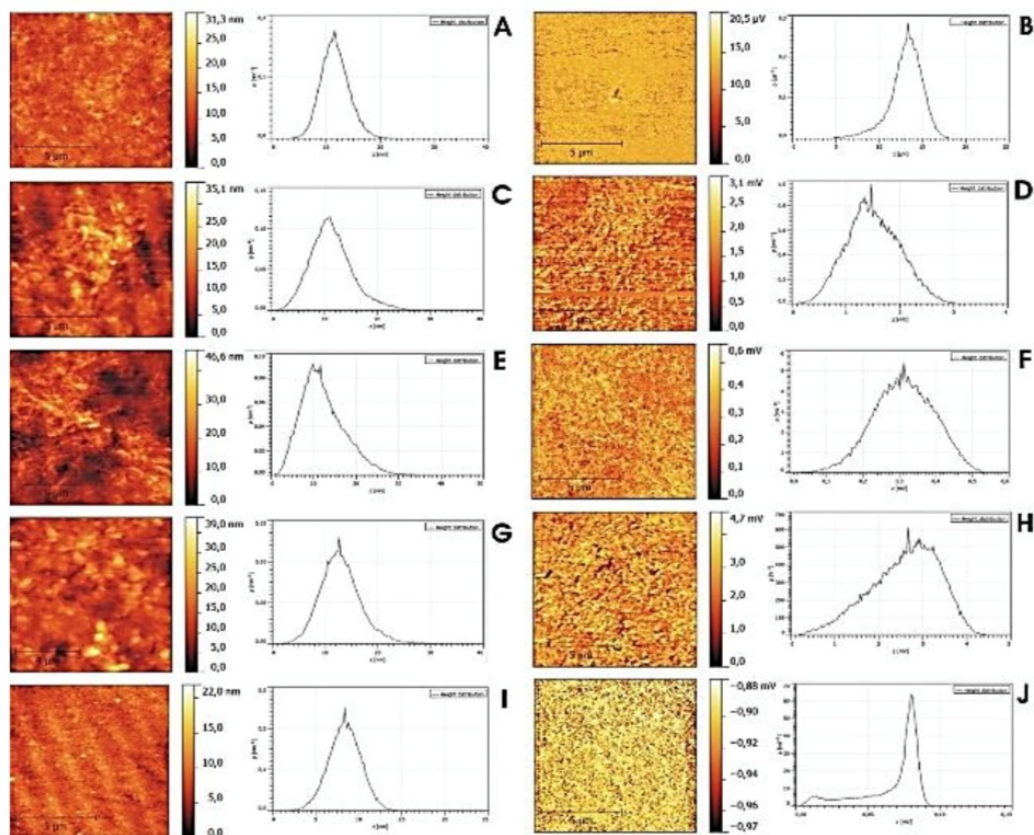
Figure 7. Local electrical measurements of the reduced graphene oxide (rGO) films deposited onto glass substrates were performed by using conductive AFM (c-AFM) using a TT-AFM (AFM WorkshopTM) microscope. C-AFM measurement was carried out by directly applying the bias voltage between the tip and the rGO film in contact mode. Left and right images (also histograms) at each row are the topography and conductivity analysis results, respectively, of the same surface. Images depict topographical and electrical maps, while histograms display height and current distributions. A-H show analysis of 10 x 10 µm2 area on rGO films prepared with four different methods (A-B is sample prepared with method 1; C-D sample prepared with method 2; E-F sample prepared with method 3; G-H sample prepared with method 4), while I-J are images of indium tin oxide (ITO) substrate (taken from ref. 19).

One more AFM technology noteworthy for battery research is conductive AFM (C-AFM) which allows nanoscale electrical characterization of surfaces. Characteristics that C-AFM can measure include local conductivity, charge distribution, and current-voltage (I-V) curves. A thing of beauty that AFM achieves here is that it is possible to simultaneously obtain a topography image and an electrical conductivity map of the same surface. Thus you can compare both images and reach conclusions about the conductivity mechanism at the nanoscale.

Iwan et al. used the C-AFM technique for nano electrical characterization of reduced graphene oxide (rGO) that has been reported in the literature as both an anode and cathode material.[xix] The researchers tested various methods for the reduction of graphene oxide and studied the effect of each method on the electrical behavior of the resulting rGO surface. As shown in Fig. 7, they compared surface topography with conductivity distribution for each method. It can easily be observed from the images (Fig. 7) that the current distribution mostly matches the height distribution. Researchers obtained the most homogenous current distribution with method 1, which also yielded the most homogenous topography map (narrowest histogram curve). Homogeneity of the surface regarding conductivity could be essential for battery electrodes. In summary, c-AFM was suitable for identifying the proper synthesis method that generates the optimal electrode surface.

Although bulk characterization methods such as cyclic voltammetry give valuable information about the performance of batteries, clarifying their underlying working principle require techniques that can make electrochemical measurements at the nanoscale. KPFM (Kelvin probe force microscopy), an AFM-based approach that can measure the work function of material surfaces, fits that requirement.

Work function is a material surface property and is defined as the energy required to remove an electron from a solid surface. A material with a lower work function requires less energy to release its electron or, in other words, do it more readily. And, when two materials with different work functions contact each other, electrons travel from the one with the lower work function to the next. That could affect the chemical stability of electrodes and the performance of batteries, such as lifespan and charge cycle.[xx] Therefore, measurement of this property for electrode materials and solid electrolytes could not be more relevant for understanding how they work and improving their performances.

KPFM allows for scanning the surface and measuring work function "pixel by pixel," hence giving local information. Furthermore, it can be operated in situ, such as when the battery is charging or discharging, and reveal how electrochemical reactions proceed (e.g., uniformly or non-uniformly). Additionally, it allows delineating the mechanism of defect formation and performance loss upon charge-discharge cycles.
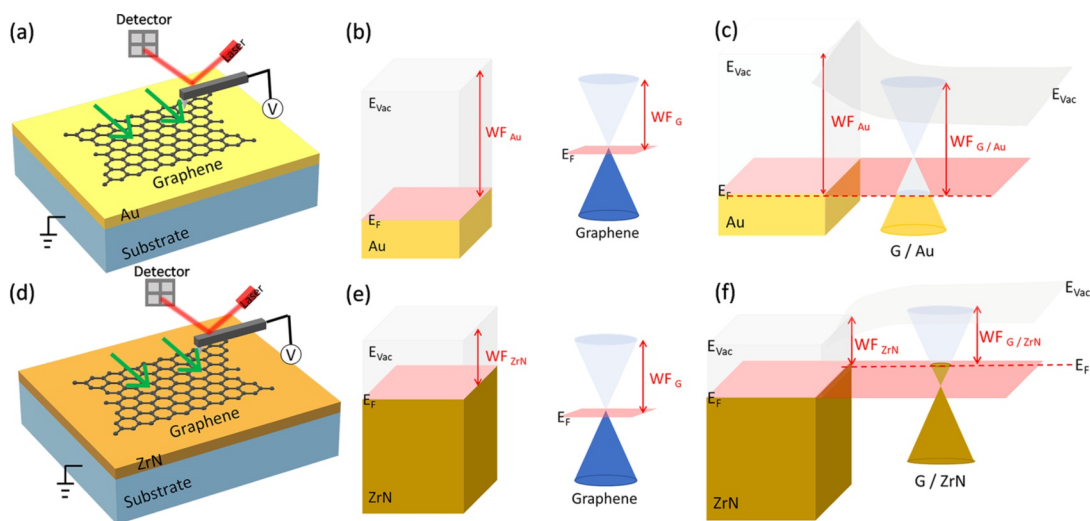
Figure 8. *Schematics of the KPFM method and the equilibrium band diagrams of graphene-on-metal (G/M) heterostructures (taken from ref. 21). Work functions (WF) of G/Au (a) and G/ZrN (b) were measured by using the KPFM method. Schematics of the equilibrium band diagrams are for graphene, Au, and ZrN alone based on measured work functions via KPFM (b, e). Schematics of the equilibrium band diagrams for G/Au and G/ZrN structures (c, f).*

Recently Yu et al. described the use of KPFM for evaluating the changes in work functions of gold and zirconium nitride (ZrN) surfaces after doping graphene onto them.[xxi] First, they visualized nanoscale variation of surface potential difference (between probe and surface) for 'graphene-on-metal (G/M) heterostructures.' Then, they used it to calculate the work functions for doped and undoped surfaces (Fig. 8, 9). Data indicated that graphene addition increased surface potential for gold surface and decreased it for ZrN surface (Fig. 9). As the potential difference between a surface and the probe becomes high, the work function gets lower as the electrons are readier now to leave the surface.

Therefore, the G/Au surface had a lower work function than the Au surface (Fig. 8a-c). Conversely, the G/ZrN surface had a higher work function than the ZrN surface (Fig. 8d-f).
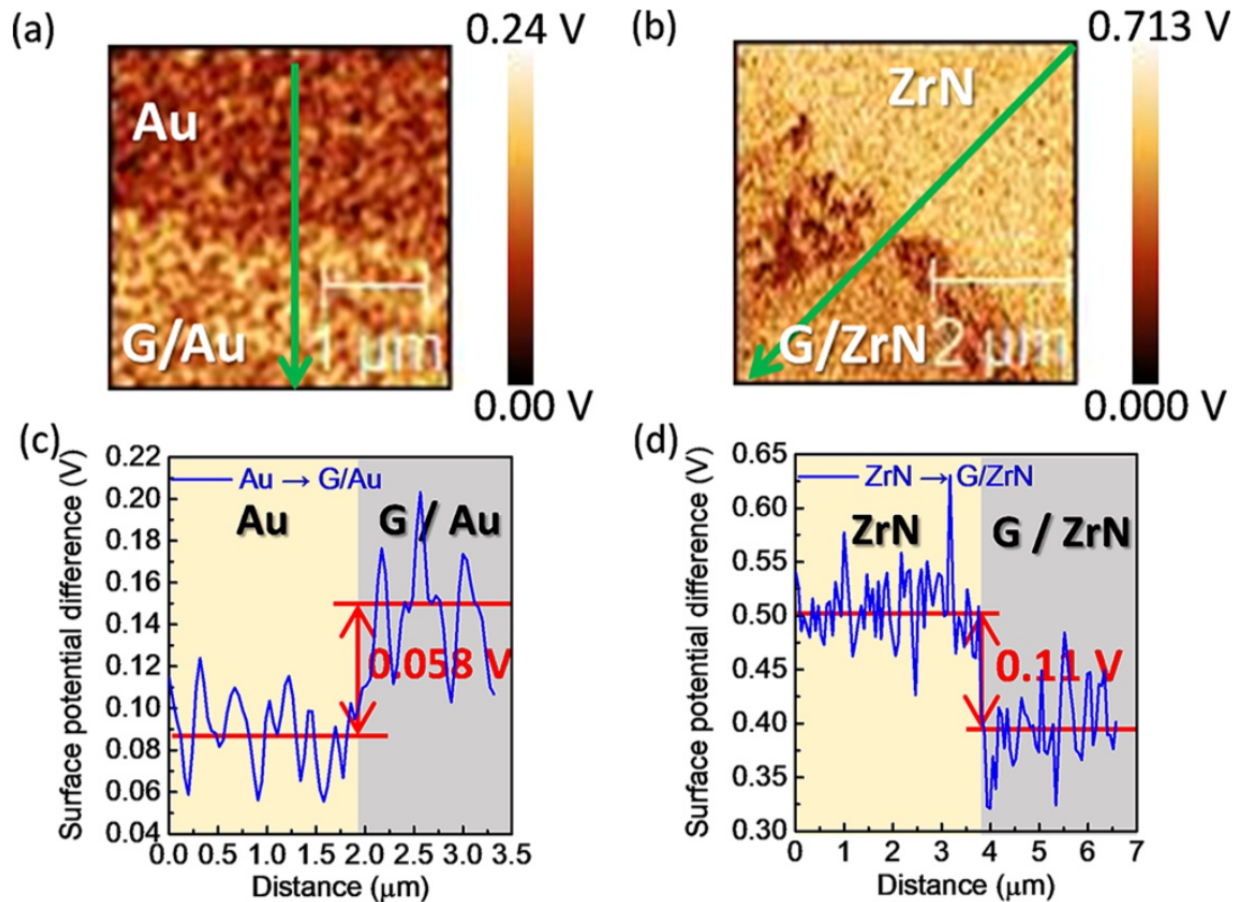
Figure 9. KPFM technique allowed researchers to obtain surface potential difference maps of graphene-on-metal (G/M) heterostructures. Nanoscale variation of potential difference between an AFM probe and the surface for Au – G/Au (a) and ZrN – G/ZrN (b) structures were captured. Surface potential variations along the green arrows shown on images in parts a and b are illustrated graphically in c and d. KPFM imaging was carried out by using TT-2 AFM (AFM WorkshopTM) in noncontact mode (taken from ref. 21).

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