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# A Study of the Porosity of Activated Carbons Using the Scanning Electron Microscope

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## 1. Introduction

The earliest mention of the significance of porosity in the performance of activated carbons is generally attributed to the French chemist Antoine-Alexandre-Brutus Bussy who in a 1822 publication suggested that porosity was important to the adsorptive properties of activated carbons. Since then a lot of research has gone into elucidating the nature of porosity of activated carbons, its development and measurement. In particular, a great deal of research has been spent on understanding factors that affect the development of porosity and how to model the porosity in terms of these factors. Similarly, much effort has gone into identifying accurate methods and procedures for characterizing activated carbons in general and particularly its pore structure. The continued interest in these research is because of the continued use and importance of activated carbons in industry and an unrelenting pursuit to improve on its performance. Characterization of porosity is often done indirectly by measurement of secondary data from which the requisite pore parameters are estimated. But direct methods also exist for characterizing the pore structure of activated carbons. Methods such as optical microscopy and scanning electron microscopy (SEM), in view of their ability to directly view the micro-structure of activated carbons have demonstrated enormous potential for use in the study and characterization of activated carbons [ Manocha et al., 2010; Lazslo et al., 2009; Achaw & Afrane, 2008]. However, this latter approach has only been applied in a very limited capacity in the past. Rather, industry and researchers alike continue to rely on the indirect methods to determine and quantify porosity in activated carbons. The indirect methods calculate activated carbon characteristics from measurement of other parameters that are generally thought to relate to the properties of interest. Adsorption measurements and related mathematical models wherein information regarding the pore structure of an activated carbon is determined are the most commonly used amongst the indirect methods. Porosity measurements using this approach extracts such pore characteristics as pore volume, surface area, pore size distribution and average pore diameter based on mathematical models of the adsorption process, information on the adsorbate and an adsorption isotherm. Besides adsorption measurements, several other indirect methods also exist to estimate the pore characteristics of activated carbons. Among these are immersion calorimetry, small angle scattering of X-rays (SAXS), small angle scattering of neutrons (SANS), and mercury porosimetry[Rigby & Edler, 2002; Stoeckli et al, 2002; Daley et. al., 1996].

The weakness of the indirect methods, is that they are based on models that do not always match with observed behavior of activated carbons. Others like mercury porosimetry are based on very simplified descriptions of the pore structure of activated carbons that are greatly deviated from pores observed directly using direct methods. Not surprisingly, pore characteristics estimated based on two different such models or methods rarely agree [Rodriguez-Reinoso and Linares-Solano, 1989]. The weaknesses notwithstanding, the indirect methods have thus far served a useful purpose of providing a framework for assessing and comparing activated carbons. In particular, they have provided a useful vehicle for predicting and evaluating the performance of these materials for industrial and other applications. The drawbacks of these methods, however, have meant that more consistent and reliable methods continue to be searched to measure the characteristics of activated carbons. The direct methods represent a viable option in that regard. Direct methods allow the direct viewing of the topography of the activated carbon surfaces which makes possible improved description of activated carbon properties such as pore shapes and pore orientation. When coupled with other methods or instrumentations, such as computerized image analysis, it is possible to estimate the pore characteristics of activated carbons more accurately. Again, these methods make possible a visual follow up of the stages of activated carbon manufacture which in turn makes possible the tracking of the changes that a precursor material goes through in forming an activated carbon. It thus offers enormous possibilities of shedding light on the pore development processes than hitherto known [Achaw & Afrane, 2008]. Already, in areas such as materials engineering, biology and medical sciences, the SEM has been extensively used to study and characterize the microstructure of substances [Chira et al., 2009; Vaishali et al., 2008; Chung, et al., 2008; Kamran, 1997]. The purpose of this chapter is to discuss the potential use of the SEM in understanding porosity development in activated carbon and pore structure characterization using micrographs of coconut shells at different stages during the manufacture of coconut shell-based activated carbons.

## **2. Tracking porosity development using the scanning electron microscope**

To better control porosity in activated carbons, it is essential that its development during its preparation be well understood. It is now generally known that porosity in activated carbons is derived from three main sources, namely, the inherent cellular structure of the precursor material, the conditions extant during the preparation of activated carbons and the composition of the precursor material [Heschel & Klose, 1995; Raveendran et al., 1995; Evans & Marsh, 1979;]. How these factors combine to produce an activated carbon of a given specification has been and continues to be a subject of intense research. This continued search is borne out of the need to find newer applications for activated carbons and an unending desire to improve on the performance of activated carbons in such operations like filtration, gas and metal adsorption and separation, gas storage, and finally in water purification. In all these applications the performance of an activated carbon depends as much on the total pore volume as it does on the pore size distribution, the prevalence of a certain pore size regime, and the surface chemistry of the carbon. For instance, during operations involving molecular sieve activated carbons, that pore size characteristics is required that permits the separation of two or any number of molecules of differing molecular sizes. Achieving this kind of performance demands a special design of the pore structure of activated carbons. This in turn demands not only an understanding of how

porosity in activated carbons is developed but an additional insight into how to control its development. The different pore sizes play unique roles during activated carbon application. Indeed, the classification of the pores in activated carbons into micropores, mesopores and macropores is based more on the varied behavior of admolecules in these pore regimes than on the actual sizes of the pores. Thus, more than the total pore volume or total surface area of the activated carbons, the fraction of the total pore volume or surface area due to the various sizes of pores is of utmost importance. Again, understanding this development is essential for the design of models to describe the performance of activated carbons and the prediction of activated carbon behavior. According to IUPAC nomenclature [Sing, et al., 1985], micropores are those pores with width less than 2 nm. The micropores play the key role of providing the bulk of the surface involved in adsorption, which is the basis of many applications of activated carbons. The mesopores are wider than the micropores and have pore widths in the range 2 nm to 50 nm. The mesopores also play a role in adsorption albeit on a reduced scale compared to the micropores. The role of the mesopores becomes more important during the adsorption of large molecules that cannot be accommodated in the micropores. Finally, there are the macropores which have much larger pore sizes and which play the important role of being the conduits through which access to the interior of the activated carbon and hence to the mesopores and micropores are achieved. They are generally considered as being part of the external surface of the activated carbon. The macropores have size greater than 50 nm.

Pores in activated carbons are areas of zero electron density in the carbon matrix. These constitute volume elements distributed throughout the particle and possess varied sizes and shapes. The individual volume elements are connected with each other through open channels which are themselves also volume elements. The volume elements are now known to originate from several sources. First, there are those whose source can be traced directly to the primary pore structure of the precursor material. Another group of pores are created as a result of the imperfections that arise from the arrangements of the lamellar constituent molecules (LCM) which are the building blocks of activated carbons. The LCM are layers of sheets which are made up of interconnected aromatic rings. They are formed when the precursor materials are subjected to heat treatment at the appropriate temperature and conditions [Bryne & Marsh, 1995; Evans & Marsh, 1995]. The imperfect arrangements of the LCM creates space in-between parallel layers of the molecules. Volume elements are also created when parts of the LCM are reacted away during contact with agents used in the activation process. The volume elements arising as a result of LCM arrangements and reactions constitute microporosity, and to a lesser extent mesoporosity in the activated carbon. The microporosity confers on activated carbons the unique ability to adsorb large quantities of a diverse range of molecules which makes activated carbons so useful in separation processes and other applications.

The LCM and the accompanying microporosity are formed when the original cellular structure of the precursor material undergoes molecular transformation and reconstitution. During heat treatment of the precursor material a number of physical and chemical processes occur that culminate in the final activated carbon pore structure. Among these, first, moisture and other volatile constituents of the precursor material escape leaving voids that may be later transformed or retain themselves in the final activated carbon product. Secondly, the macromolecules of the precursor material breakdown, lose mostly oxygen and

hydrogen and reconstitute into aromatic rings which become the building blocks of the LCM. The new constituent molecules form to enclose the vacancies left by the escaping elements and molecules. These vacant lots also constitute porosity in activated carbons. The transformations are initiated during the pyrolysis of the precursor material and are continued and enhanced during the subsequent activation stage. The loss of volatile matter from the precursor materials occurs at all temperatures but aromatization of the material occurs at temperatures in excess of 700°C. Another important process occurs during the activation process to create new pores or enhance existing pores formed during the pyrolysis step. During activation, activation agents react with the carbon skeleton to create new pores or enlarge existing ones. It is also at the activation stage that other phenomena that facilitate pore creation manifest. For instance, inherent mineral matter such as alkali metals in the precursor material catalyze the pore formation process leading to such phenomena as pitting, channeling and pore enlargement [Bryne & Marsh, 1995]. Pores are also developed as a result of thermal stress on the cellular structure of the precursor material. This stress leads to the development of cracks, crevices, slits, fissures, and all manner of openings in the matrix of the ultimate carbon material. The events leading to the formation of pores occur mainly at the micro and sub micro levels and most of the products of the process such as LCM and associated carbon rings are hardly, directly, observable even with the most powerful of electron microscopes available today. As such these processes have most remained in the realm of theoretical discourse. However, there are other manifestations of these transformations that with the appropriate tools are observable. Using the SEM it has been possible to view images of some of the phenomena that engender porosity development in activated carbons. The ability of the SEM to distinguish objects as small as 1 nm makes it ideal for tracking the transformations happening in the precursor material during activated carbon formation. This SEM has however not been fully exploited yet for the study of porosity development in activated carbons save for the pioneering work of Achaw & Afrane, 2008. Figures 1-3 below, show SEM micrographs of sections of coconut shell at different stages during the preparation of coconut shell-based activated carbons. The images reveal details about these materials that shed useful light on aspects of porosity development in activated carbons.

Micrographs in Figures 1 - 3 reveal details of activated porosity development that, previously, has only been a matter of theoretical discourse. Samples for the SEM micrographs used in this study were prepared by cutting sections of well dried coconut shell (raw coconut shells, carbonized shells or coconut shell-based activated carbon) and mounting a on specimen stub with the help of a conductive silver adhesive. The specimen surfaces were thereafter sputter coated with a thin film of silver, placed in the sample holder and viewed with a Zeiss DSM 962 electron microscope. A look at Figures 1 and 2 suggest that the original cellular structure of the coconut shells as seen from the transverse section are largely maintained albeit in a modified form following carbonization. In Figure 1 the largely isolated cylindrical units, see positions labeled A and B, has walls made up of layers of thin sheets. In Figure 2, these units seen in Figure 1 have joined together at the walls into a singular solid matrix interspersed with pores. The sheets of the walls are no longer visible in Figure 2. The joining of the walls and the fusing together of the sheets of the walls suggests a profound transformation at the molecular level in the shell during the pyrolysis.



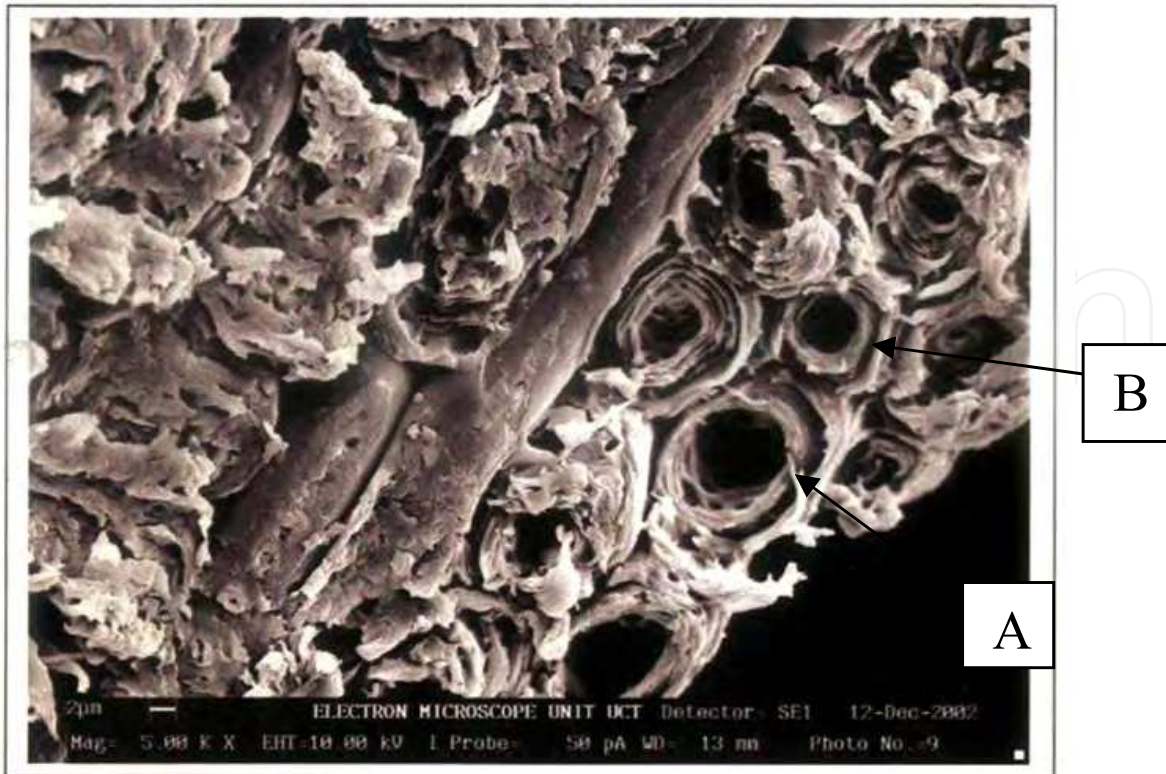


Fig. 1. Micrograph of surface of transverse section of raw coconut shell.  
Source: Achaw & Afrane, 2008

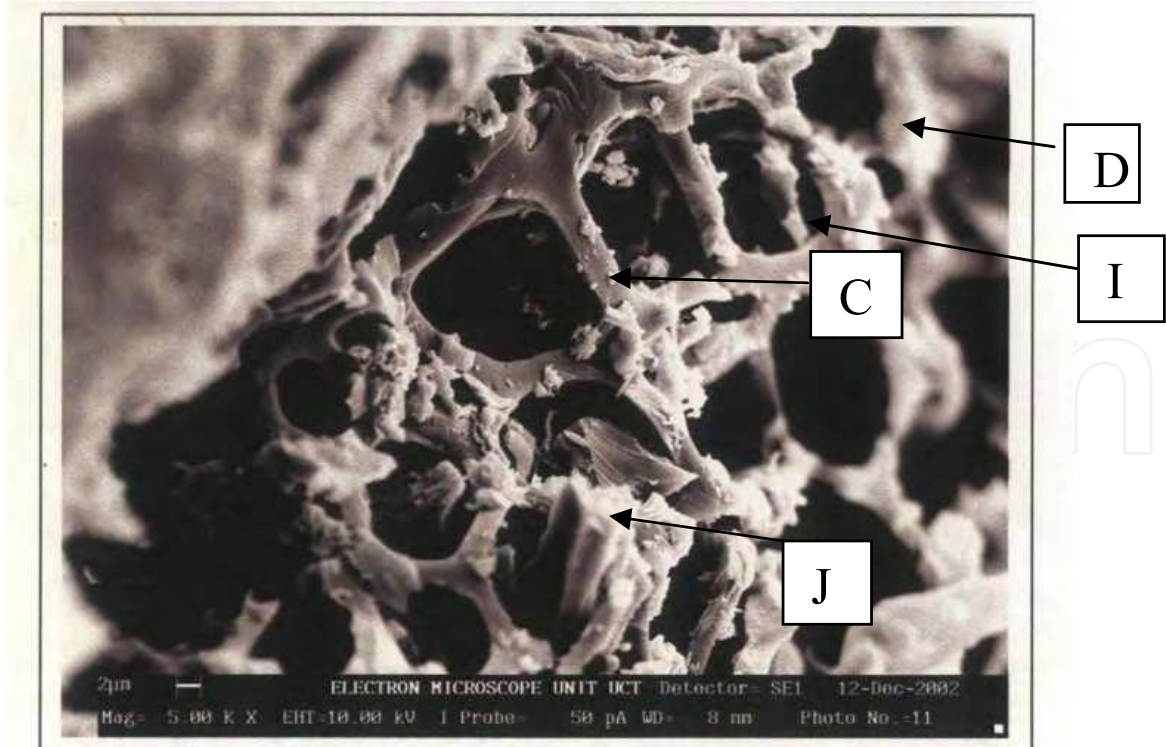


Fig. 2. Micrograph of surface of transverse section of carbonized coconut shell  
Source: Achaw & Afrane, 2008

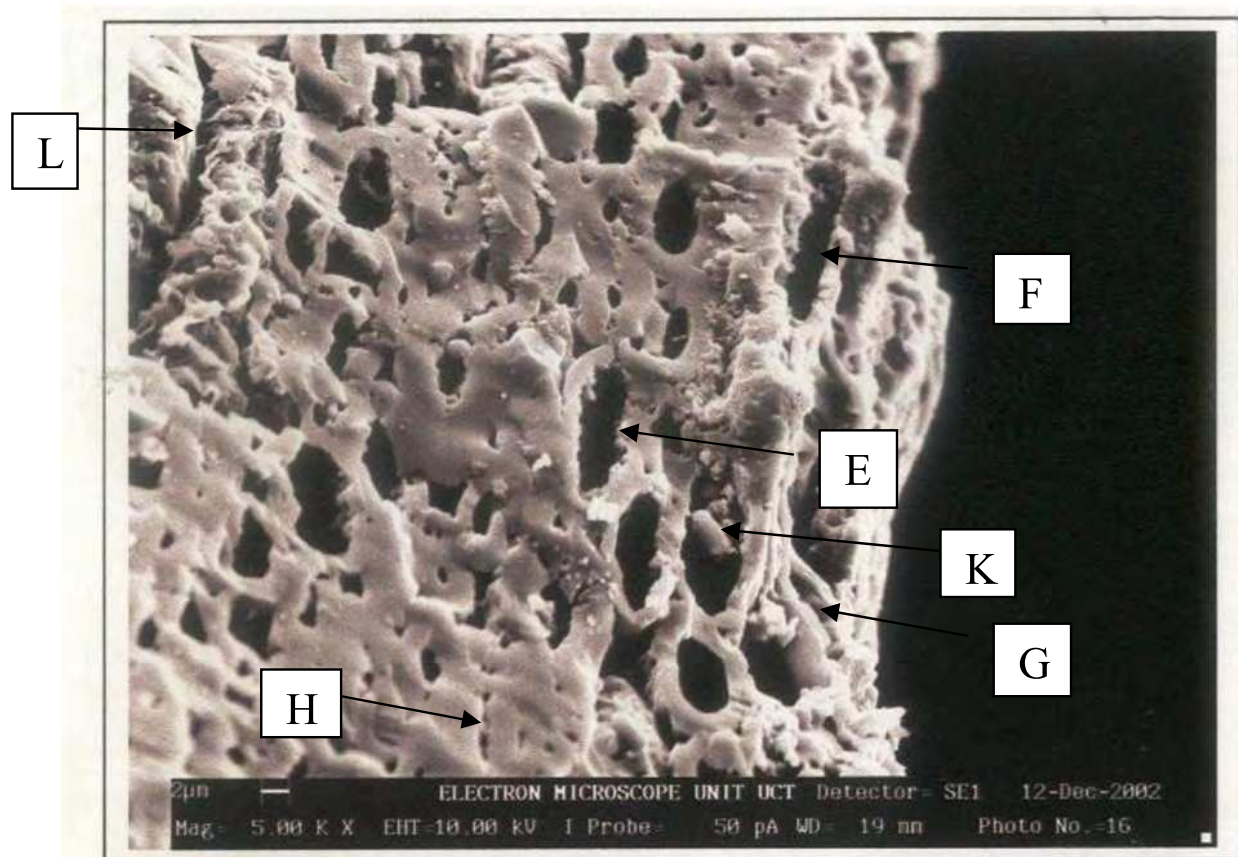


Fig. 3. Micrograph of transverse section of coconut shell-based activated carbon  
Source: *Achaw & Afrane, 2008*

Notice that the cylindrical units in Figure 1 has deformed into all manner of shapes after the pyrolysis, see Figure 2, positions marked C and D. The transformation of the pores continues to the activation stage, see positions marked E and F in Figure 3, where what were originally cylindrical shape has now become partially flattened cylinder. The micrograph of the activated carbon further demonstrates transformation of the matrix of the shell as a result of continued heating during the activation. The narrowing of the pore widths suggest a kind of deformation where the matrix softens and walls of the pores give way and close in on each other. Notice further that as a result of this deformation, some of the walls have completely fallen in on each other resulting in a complete zipped up of the pores, see positions marked G and H. The transformations suggest that the carbon matrix passes through a plastic phase as a result of the thermal treatment. Another phenomena observable from these micrographs is the preponderance of foreign materials in the pores of the carbonized product, see positions marked I and J on Figure 2, and the almost lack of these materials in the activated carbon of Figure 3. This means that the activation process serves the additional purpose of cleaning foreign materials from the carbon besides the creation of pores. It is nonetheless noteworthy that even at the activated carbon stage some pores still remain blocked by foreign material, see position marked K in Figure 3. This last observation is an indication that the activation process was not complete. It is anticipated that these foreign materials would be completely cleared at the end of the activation process. Yet another important feature of these micrographs is the position marked L on Figure 3 which is a crack in the carbon matrix probably developed as a result of thermal stress on the carbon



matrix due to temperature changes in the activation process. Such cracks contribute to the overall surface of the activated carbon and as such are important. Yet discourse on porosity development of activated carbons often ignore these cracks.

### 3. Characterization of activated carbons

Characterization of activated carbons is driven by the need to have qualitative and quantitative information which serve as the basis for comparison and selection of activated carbons for specific applications. Such data are also useful for modeling the behavior and performance of activated carbons. Furthermore, characterization provides feedback for use in the design and preparation of activated carbons. The characteristics often measured are density, abrasion resistance, surface area, average pore size, pore size distribution, pore shape, pore volume, and the surface chemistry of the carbon. Whilst there are well established standard methods for measuring the density and abrasion resistance, scientists and industry are still grappling with what accurate methods to use for measuring the others. Most current methods estimate these parameters indirectly from measurements of secondary data on the activated carbons. As a result there are still concerns with the accuracy of values determined for these parameters. The most popular method for characterizing activated carbons is through the measurement of adsorption data and application of mathematical models that relate the adsorption data to such characteristics as pore volume of the adsorbent and the properties of the adsorptive. Other indirect methods, namely, mercury porosimetry, immersion calorimetry, small angle scattering of X-rays (SAXS), neutrons (SANS), high-resolution transmission electron microscopy are also sometimes used to determine the characteristics of activated carbons. Then there are direct methods that hold enormous potential for characterizing activated carbons but which use are rarely mentioned in activated carbon literature. These latter methods are mainly the microscopic methods which enable the observation of micro- and sub-micro features of activated carbons and hence the direct measurement of these features. These microscopic methods are optical microscopy and the SEM.

#### 3.1 Adsorption methods of characterizing activated carbons

These methods almost invariably combine the adsorption isotherm of a given adsorbate-adsorbent system and a theoretical or empirical model of the adsorption process to estimate the characteristics of activated carbons [Machnikowski, et al., 2010; Noor & Nawi, 2008; Lozano-Castello et al., 2004; Stoeckli et al., 2002; Stoeckli et al., 2001 Yuna et al., 2001; Rodriguez-Reinoso, 1989]. Most commercial sorption equipment estimate activated carbon data using in-built software based on one version or the other of this approach. Of historical importance is the Langmuir model [ Gregg & Sing, 1982] which was first developed in 1916 to describe adsorption behavior on solid adsorbents in general. The model relates the adsorption of molecules in a gaseous medium onto a solid surface to the gas pressure above the solid at a fixed temperature and can be expressed mathematically as

$$\frac{P}{V} = \frac{P}{V_m} + \frac{1}{bV_m} \quad (1)$$

$V$  is the equilibrium adsorbed amount ( $\text{mmol g}^{-1}$ ) of the adsorbate per unit mass of the adsorbent at a pressure  $P$ .  $V_m$  is the amount of gas required for monolayer coverage of the



adsorbent ( $\text{mmol g}^{-1}$ ), and  $b$  is a constant whose value depends on the temperature. A linear plot of equation (1) allows  $V_m$  to be evaluated from the gradient and hence the adsorbent's surface area from the relation

$$S = V_m L \sigma \quad (2)$$

$S$  is the total surface area of the adsorbent ( $\text{m}^2\text{g}^{-1}$ ),  $L$  is Avogadro's number and  $\sigma$  is the projected surface area of the adsorbate molecule.  $S$  is the sum total of pore surfaces and external (non-pore) surface of the adsorbent. Equation (1) is based on the assumption that i) there is a mono-layer adsorption, ii) there are no adsorbate-adsorbate interactions on the adsorbent surface, iii) the adsorbent has a homogeneous surface, iv) all adsorption sites on the adsorbent are equivalent and, v) the adsorbing gas adsorbs into an immobile state.

The Langmuir's model has been found to be of limited applications for activated carbons. In particular, activated carbon surfaces are rarely homogeneous. Generally, the assumptions have been found not to be consistent with observations therefore the Langmuir model is rarely used to characterize activated carbons. Consequently, other relatively more accurate models of adsorption are often used. One such model is the Braunnauer, Emmett and Teller (BET) model [Sing et. al., 1985]. The BET method has a much wider application and is most often used to interpret adsorption isotherms obtained using Nitrogen at 77K as the adsorbate. The model is an improvement on the Langmuir model in that it can account for multilayer adsorption. It relates the adsorption pressure and the volume of the adsorbed adsorbate according to the equation

$$\frac{p}{V(p^0 - p)} = \frac{1}{V_{mc}} + \frac{c - 1}{V_{mc}} \frac{p}{p^0} \quad (3)$$

where

$$c = \exp\left(\frac{(\Delta H_A - \Delta H_L)}{RT}\right) \quad (4)$$

In equation (3),  $V_{mc}$  is the monolayer capacity of the adsorbent,  $p^0$  is the saturation vapour pressure of the adsorbate gas,  $p$  is the pressure of the gas, and  $c$  is a constant which is exponentially related to the heat of first layer adsorption.  $\Delta H_A$  is the heat of adsorption,  $\Delta H_L$  is the heat of liquefaction of the adsorption fluid,  $T$  is the temperature, and  $R$  is the gas constant. A linear plot of equation (3) allows  $V_{mc}$  to be determined from the intercept and from which the surface area of the activated carbon can be estimated using equation (2). The BET method has found a number of applications in adsorption studies and is especially used in the determination of the surface areas of adsorbents including activated carbons. Even so, the BET equation is unable to account for adsorption in a number of instances. For activated carbons equation (3) is only linear at  $p/p^0 < 0.1$ . This introduces error into the measurement of those pores for which adsorption is possible at pressures for which  $p/p^0 > 0.1$ . Secondly, the calculation of the adsorbent surface area using equation (2) requires knowledge of the projected surface area of the adsorbate molecule, in this case Nitrogen. This in turn requires that the adsorbate molecules (Nitrogen) be in a close packed, monolayer coverage on the adsorbent. The use of the method implicitly assumes that the value estimated for  $V_{mc}$  is necessarily accurate and that  $\sigma$  is constant for the adsorbate under all conditions. Further,

adsorption in micropores is characterized more by pore filling than by surface coverage. As such, the application of the BET method does not always yield the correct result for the surface area of activated carbons, especially if they are predominantly microporous.

Probably more accurate among the adsorption methods for the determination of pore characteristics of activated carbons is the Dubnin-Raduskevitch (DR) equation and its improved and more versatile version, the Dubnin-Astakov (DA) equation [Dubnin & Raduskevitch, 1947; Dubnin, 1989; Carrasco-Merin et al., 1996; Gil, 1998]. The DR equation is premised on the assumption that adsorption in micropores occurs by pore filling rather than by physical adsorption on the surface of the micropores. The equation relates the volume of pores,  $W$ , filled by an adsorbate at a given temperature  $T$  and relative pressure  $p/p^o$  and other parameters of the adsorption system as

$$W = W_o \exp\left[-\left(\frac{A}{\beta E_o}\right)^2\right] \quad (5)$$

where  $W_o$  is the total volume of the micropores,  $E_o$  is the characteristic energy, and  $\beta$  is the affinity coefficient. Both  $E_o$  and  $\beta$  are system dependent. The differential molar work of adsorption on the adsorbent,  $A$ , is further defined as

$$A = RT \frac{p}{p^o} \quad (6)$$

For slit-shaped pores, a relationship exists between  $E_o$  and the average micropore width  $\bar{L}$  as

$$\bar{L}(nm) = 10.8(E_o - 11.4) \quad (7)$$

The DR equation has a narrow range of application as it corresponds to mostly Type I isotherms. The Dubnin-Astakov (DA) equation which is a modification of the DR equation and which is applicable to a wide range of microporous carbons is therefore preferred. The generalized form of the DA equation is

$$W = W_o \exp\left[-\left(\frac{A}{\beta E_o}\right)^n\right] \quad (8)$$

When  $n=2$ , equation (8) becomes equal to the DR equation. Values of  $n$  between 1 and 4 are observed for most carbon adsorbents,  $n > 2$  for molecular sieve carbons or carbons with highly homogeneous and small micropores,  $n < 2$  for strongly activated carbons and heterogeneous micropore carbons. For monodisperse carbons,  $n=3$  and for strongly heterogeneous carbons  $n=2$  [Carrasco-Merin et al., 1996].

### 3.2 Characterization of activated carbons with the scanning electron microscope

In the areas of porosity development and characterization of activated carbons, a number of issues still remain unresolved. The current state of knowledge has not been able to address all observed behavior and performance of activated carbons. For instance, to what extent does thermal stresses on the carbon matrix during pyrolysis affect porosity development.

How realistic is the often used slit-shaped pore model in describing activated carbons. Similarly, in characterizing activated carbons the often used methods such as adsorption measurement and mercury porosimetry all rely on secondary data and mathematical models to estimate pore characteristics. But these methods are fraught with a number of drawbacks. In these methods, only those pores can be characterized that the adsorbate molecules could have access to. Also the mathematical models of adsorption which are the basis of estimating pore characteristics are based on assumptions most of which do not match with observations. Adsorption measurements in particular have other drawbacks that affect the accuracy of parameters estimated. For instance, phenomena such as activated diffusion and gate effects introduce errors into adsorption based estimates of pore parameters. Equally, idealized pore models such as the cylindrical or slit-shape pore which are the basis of a number of methods for estimating average pore width of activated carbons are too simplistic in the face of the observed complex nature of porosity in activated carbons. Then again some of the pore parameters are not at all amenable to estimation by the indirect methods. Such parameters like pore shape, pore location and distribution, and pore orientation have all eluded estimation by the indirect methods. These parameters nonetheless have important consequences on modeling and prediction of performance characteristics of activated carbons and therefore are worth estimating or measuring.

Direct methods, particularly, microscopy offers an alternative approach to resolving most of the drawbacks of the indirect methods. Using microscopy, it is possible to observe the micro and submicro-features of activated carbons directly and therefore makes possible a proper qualitative and quantitative description of its characteristics [Ito & Aguiar, 2009; Daley et al., 1996; Tomlinson, et al., 1995; Hefter, J., 1987; Ball & McCartney, 1981]. There are two types of this method, namely, optical microscopy which has a resolution of about 1  $\mu\text{m}$  and electron microscopy whose resolution is much greater and in the range of about 1.5 nm and which can achieve a magnification of about 2,000,000x. The SEM is one version of the electron microscopy which uses a beam of electrons to scan the surface of a specimen and makes possible the direct observation of its surface features at the micro and submicro levels. Due to the huge magnifications and impressive resolutions achievable with the SEM it has been used in many areas of science and industry, particularly in materials engineering, biological and medical sciences for the study and characterization of the micro-structure of substances. It use provides an avenue to resolve some of the yet unresolved issues in activated carbon porosity development and characterization. The SEM functions exactly as its optical counterparts except that it uses a focused beam of electrons instead of light to "image" a specimen and gain information about its structure and composition. The SEM can yield information about the topography (surface features of an object), morphology (shape and size of the particles making up the surface of an object), composition (the elements that the object is composed of and the relative amounts of these) and crystallographic information (how the atoms are arranged in the object). This ability makes the SEM a hugely useful instrument for the study of activated carbons. The topographic information attainable using the SEM allows that surface features such as pore characteristics, the description of which has been a major preoccupation of activated carbon chemists, to be studied and measured directly from SEM micrographs. Also SEM's ability to reveal compositional details of a specimen makes it a potent instrument for studying the surface chemistry of activated carbons. Other features of the SEM that make it a unique instrument for studying activated carbons include its ability to reveal details of a sample less than 1 nm in size. This means

that, in principle, even micropores could be exposed for study by SEM micrographs. Again, due to the very narrow electron beam employed, SEM micrographs have a large depth of field that yields a pseudo three-dimensional appearance useful for understanding the surface structure of a sample. Figures 4-7 are examples of SEM micrographs that reveal details of activated carbons that only the direct methods can show.



Fig. 4. Micrograph of outer surface of raw coconut shell  
Source: Achaw & Afrane, 2008

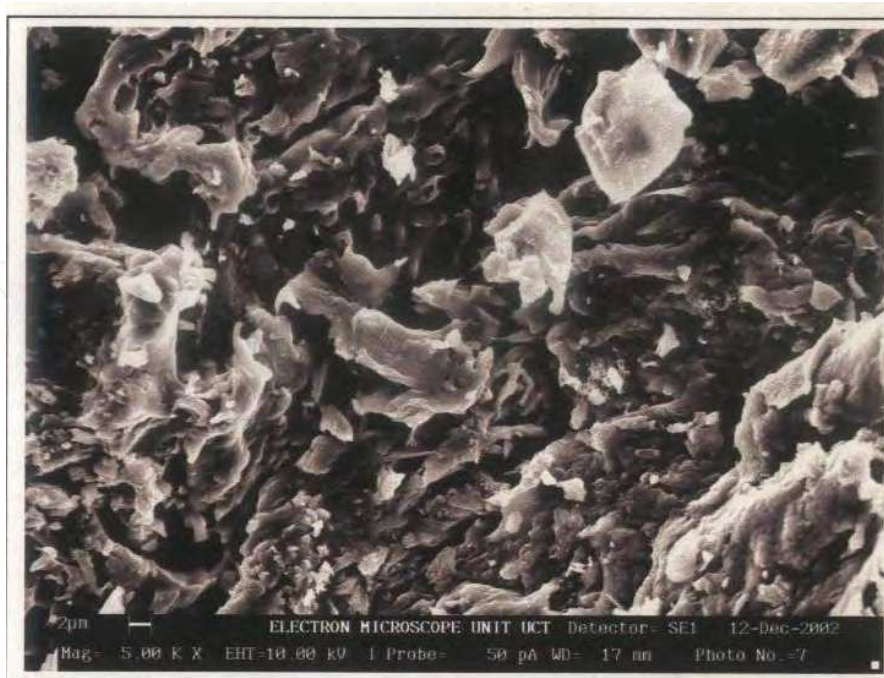


Fig. 5. Micrograph of outer surface of carbonized coconut shell.  
Source: Achaw & Afrane, 2008



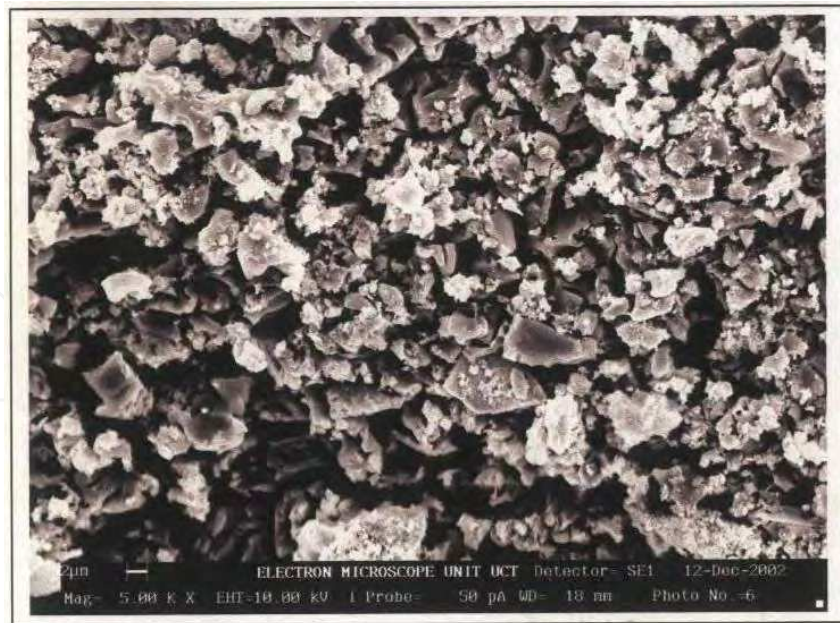


Fig. 6. Micrograph of outer surface of coconut shell-based activated carbon  
 Source: Achaw & Afrane, 2008

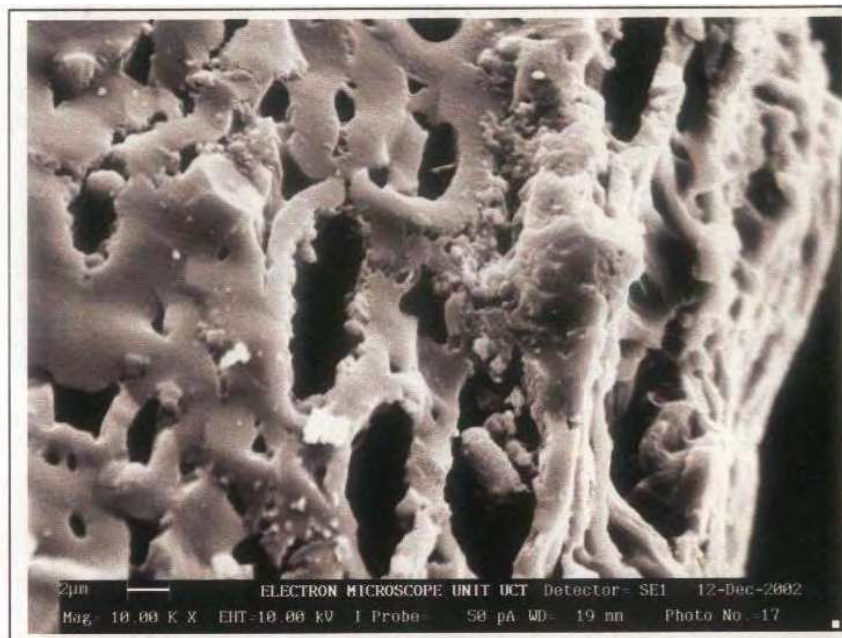


Fig. 7. A Micrograph of transverse section of coconut shell-based activated carbon  
 Source: This study

The micrographs in Figures 4-7 are all of coconut shells at different stages during the preparation of activated carbons. Figures 4-6 are micrographs of the surfaces of the outer sections of the shell. The surface features observed from these micrographs are significantly different from those seen from the corresponding micrographs of on Figures 1-3, indicating that the nature of pores seen of activated carbons depend on the sections used. Crucially, the nature of porosity observed in Figure 6 is totally different from any description of porosity previously described except in the work of Achaw and Afrane (2008). What is observed here

is a network of cracks which are more the result of thermal stress on the carbon matrix. This is totally in contrast to what was observed of the micrograph in Figure 3 which is more likely the result of re-arrangement of molecules in the carbon matrix. The observed porosity in Figure 6 further show the difficulty of defining a generalized pore structure for activated carbons. It calls to question such often used concepts as average pore size, and pore size distribution. Further, it raises questions about models associated with pore structure such as the slit-shaped model which is the basis of a number of mathematical models of adsorption in activated carbons or the cylindrical models used by mercury porosimetry and other empirical methods for estimating pore characteristics. Figures 6 & 7 are micrographs of different sections of an activated carbon. The two images clearly demonstrate the extent of inhomogeneity of the surfaces of activated carbons. Equally noteworthy of the micrographs in Figures 4-6 is the fact that there is hardly any common trend linking the structures in these micrographs. Whilst, hardly, any pore is observable at all in Figure 4, the structure in Figure 5 is fuzzy and confusing, and hardly yielding to any definition at all. Finally, even though the structure in Figure 6 has some semblance of order, it also defies any exact definition. An important observation of these micrographs is that pore development in activated carbons is as a result of several phenomena. Particularly, it seems that thermal stress plays an important role in pore development in these materials than previously thought. The foregoing observations demonstrate the strength of SEM in studying activated carbons.

#### 4. The scanning electron microscope

The main features of the SEM are an electron source which provides the electrons that interact with the material to be examined, an arrangement of metal apertures, magnetic lenses and scanning coils or deflectors plates that confines, focuses and turns the beam of electrons into a thin and focused monochromatic beam which is accelerated towards the sample and which irradiates the specimen in a raster fashion [Goldstein, J et al., 2003; Reimer, L, 1998]. The interaction of the electrons with the specimen initiates a number of reactions inside the sample which results in the generation of signals which are taken advantage of to gain information about the sample. The SEM imaging process involves four major steps. These include sample preparation, the specimen scanning process, image formation and image analysis. The kind of preparation required of the sample depends on whether it is electrically conducting or not. Electrically conducting samples, for instance metals, only require minimal sample preparation prior to mounting on a sample stub for scanning and imaging. Non-conductive specimens such as activated carbons, however, must first be made conducting before mounting for study. Otherwise, these tend to charge when scanned by the electron beam leading to scanning faults and other image artifacts. Non-conducting samples are therefore first sputter coated with an ultra-thin coating of an electrically-conducting material before imaging. Other reasons for coating the sample surface are to increase the signal and surface resolution, especially with samples of low atomic number. Some of the commonly used materials for coating samples include gold, graphite, platinum, chromium, tungsten, osmium, and indium. For biological materials it is possible to increase the conductivity without coating by impregnating them with osmium before imaging. It is also possible to image non-conducting specimen without coating by using the Environmental SEM(ESEM) or the field emission gun (FEG) SEM [Schatten & Pawley, 2008; Hardt, T. A. 1999;]. Samples for SEM study do not need to be as thin as it is

the case in optical microscopy or transmission electron microscopy (TEM). The specimen size is dictated primarily by the size of the sample chamber and must be rigidly mounted on the specimen stub. Again, in view of the applied vacuum, it is important that the sample be completely dry. Hard, dry materials such as activated carbons can be examined with little further treatment besides sputter coating.

The signals of interest in the characterization of activated carbons using the SEM are the secondary electrons whose detection and imaging gives information on the surface topography and hence on the pore structure of the activated carbons, the backscattered electrons and the X-ray radiation which give complementary information of the chemical composition of the sample surface. Whilst secondary electrons can be detected and imaged in a conventional SEM instrument, harnessing signals from the backscattered electrons and X-ray radiation requires complementary instrumentation. The secondary electrons are produced when an incident electron in the primary electron beam excites an electron in an atom of the sample and loses most of its energy in the process. The excited electron moves to the surface of the sample where it can escape if it possesses sufficient energy. In view of their low energy, only secondary electrons that are very near the surface (<10 nm) can exit the sample and be detected. The secondary electrons are detected and accelerated onto a photomultiplier from which an amplified electrical signal output is displayed as a two-dimensional intensity distribution that can be viewed and photographed on an analogue video display or converted and displayed or stored as a digital image.

Backscattered electrons (BSE) are produced when the primary electron beam hits the sample and some of the electrons are reflected or scattered back out of the specimen. The production of backscattered electrons varies directly with the specimen's atomic number. High atomic number elements backscatter electrons more strongly than low atomic number elements, and thus appear brighter in an image. BSE are therefore used to detect contrast between areas on the sample surface with different chemical compositions. This provides opportunity for examination of the chemistry of the surface of activated carbons. Dedicated backscattered electron detectors, usually either scintillator or semiconductor types are positioned above the sample to detect the backscattered electrons.

As earlier intimated, inelastic scattering, places the atoms of the sample in an excited state. The tendency therefore is for an atom to return to its ground or unexcited state. To achieve this, the atom gives off the excess energy. This may result in the production of X-rays, cathodoluminescence and Auger electrons. The relaxation energy is the fingerprint of each element in the sample. Thus detection and analysis of the relaxation energies enables the identification of the specific elements in the surface of a sample. When an SEM is equipped with energy-dispersive X-ray spectroscopy (EDX) or wavelength dispersive X-ray spectroscopy (WDS), it is possible to get information on the elemental composition on the surface of the specimen. For an activated carbon, this method can be used to study the effect on porosity development of specific elements in the carbon and generally the chemistry of the activated carbon surface [Afrane & Achaw, 2008].

#### **4.1 3D images in scanning electron microscope**

In conventional (standard) SEM a pseudo-three dimensional (3D) view of the sample surface can be observed directly. The standard SEM image is, however, really a two-dimensional (2D) structure from which mostly qualitative data is possible regarding the microstructure



of the specimen. In the study of activated carbons however, qualitative data though useful as for instance in understanding pore development phenomena, it is quantitative data on pore structure- pore sizes, pore shapes, pore surface area, and pore size distribution- that are most useful for characterization and modeling of performance and behavior. Getting quantitative data from 2D SEM images of activated carbons, however, poses a number of challenges. First, 2D SEM cannot determine three-dimensional porosity of the materials because the conventional SEM is unable to observe images of inner parts of a specimen. Then also there are the difficulties associated with getting precise descriptions or a representative pore structure in view of the otherwise complex, varied and numerous pores in the field of view of the microscope. To get quantitative data of a specimen from conventional SEM images, the practice is to convert the 2D images into 3D from which the requisite quantitative data can be measured or estimated often with the help of computerized image analysis software. A number of methods for getting 3D data from 2D images are available [Marinello et al., 2008; Spowart, 2006; Spowart et al. 2003; Alkemper and Voorhees, 2001; Lyroudia et al., 2000 ]. These include stereology, photogrammetry, photometric stereo, and the more useful serial sectioning method. An automated variation of the serial sectioning method called the focus ion beam-scanning electron microscopy (FIB-SEM) is increasingly being used in the areas of materials engineering and biological sciences to study the micro-features of substances. This last method appears to have enormous potential for use in the study and characterization of activated carbons.

In serial sectioning, 2D images of a sample are collected after a series of successive layers of equal width have been removed from the sample. Afterwards the stack of 2D data files (2D SEM images) is combined and processed in such a way that the microstructural features that are within the 3D data stack can be classified. This is most efficiently done using computerized image processing software. Serial sectioning is made up of two basic steps that are iteratively repeated until completion of the experiment. In the first step a nominally flat surface of the sample is prepared using any of a variety of methods such as cutting, polishing, ablating, etching, or sputtering. These processes remove a constant depth of material from the specimen between sections. The second step is to collect 2D characterization data after each section has been prepared, for instance by imaging with an SEM. Finally, computer software programs are used to construct a 3D array of the characterization data that can be subsequently rendered as an image or analyzed for morphological or topographical features of the sample. Using this method any micro and submicro features of the sample that can be distinguished by the SEM can also be characterized. Thus the capability of the methodology in characterizing topographical and morphological features of substances is limited only by the resolution of the SEM.

Automated serial sectioning techniques which facilitates the methodology exist for material removal and imaging. An example is the FIB-SEM which combines ion beam sectioning with SEM imaging to generate tomographic data that are well suited to characterize microstructural features of a sample in 3D via serial sectioning [Desbois et al., 2009; Orloff et al. 2003]. While less common, the FIB-SEM method has demonstrated the ability to complete 3D volumetric reconstruction at a resolution of 10 nm or better in all three dimensions. The method has been widely used for studies in materials engineering and life sciences and holds tremendous potential for characterizing the porosity of activated carbons.



## 5. Conclusion

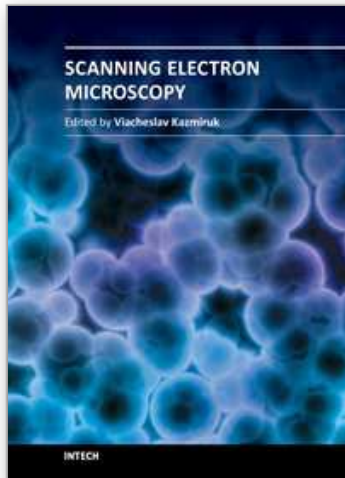
In spite of the tremendous progress in development and use of activated carbons a number of questions still remain that the conventional indirect methods of studying activated carbon are still grappling to answer. The mode of porosity development is one such area. Another area is the characterization of the porosity of activated carbons, where the existing mathematical models and methods have still not succeeded in finding accurate ways to estimate pore parameters. Recent developments in scanning electron microscopy, especially in the conversion of 2D SEM to 3D and computerized image analysis has opened avenues for improved study of porosity development and characterization of activated carbon. This potential of the SEM has not really been adequately explored for the study of activated carbons as not much work exists in the literature in that regard. However, judging from the enormous strides researchers in the areas of materials engineering and the biological sciences have made in using this methodology to identify micro and submicro-features of substances, it is anticipated that its adaptation for use in the study of activated carbons would facilitate the study of porosity development and pore characterization. The SEM micrographs shown in this work clearly demonstrate this point. The major limitation of the SEM is the level of resolution achievable with it currently. At 1.5 nm, this poses difficulty in characterizing most micropores in activated carbons. It is nonetheless hoped that continued advances in SEM instrumentation will overcome this difficulty and facilitate the use of the SEM in the study of activated carbons.

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## **Scanning Electron Microscopy**

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Today, an individual would be hard-pressed to find any science field that does not employ methods and instruments based on the use of fine focused electron and ion beams. Well instrumented and supplemented with advanced methods and techniques, SEMs provide possibilities not only of surface imaging but quantitative measurement of object topologies, local electrophysical characteristics of semiconductor structures and performing elemental analysis. Moreover, a fine focused e-beam is widely used for the creation of micro and nanostructures. The book's approach covers both theoretical and practical issues related to scanning electron microscopy. The book has 41 chapters, divided into six sections: Instrumentation, Methodology, Biology, Medicine, Material Science, Nanostructured Materials for Electronic Industry, Thin Films, Membranes, Ceramic, Geoscience, and Mineralogy. Each chapter, written by different authors, is a complete work which presupposes that readers have some background knowledge on the subject.

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