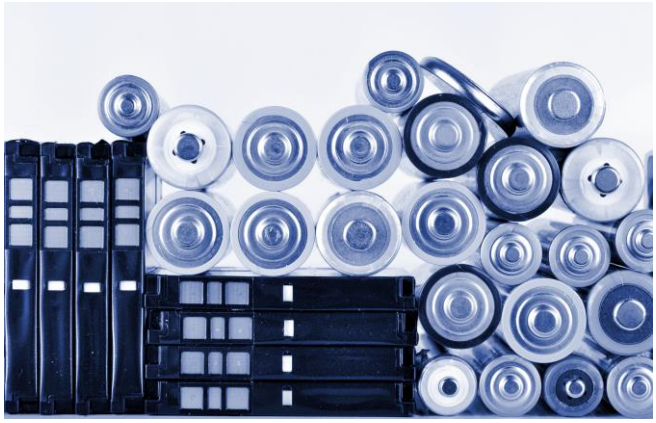
Structural Characterization of Battery Components

Relevant for: anode, cathode, battery separator, supercapacitors, battery industry, energy industry

Structural properties, such as surface area, pore size and density, of battery components can be characterized using a variety of different techniques. Examples of gas sorption, mercury intrusion, and capillary flow porometry for anode, cathode, and separator materials, among others, are discussed.



1 Introduction

Research and development professionals in the battery industry are always in search of the most efficient and safest battery technologies to fuel the energy needs of our world today and into the future. In order to optimize their design efforts, battery developers rely on accurate physical property characterization for battery components such as the anode, cathode, or separator. Important properties that guide design include surface area, pore size and pore volume, porosity (% open space), and density.

1.1 Surface Area

Surface area is a critical property for anode, cathode, and even separator materials. Surface area differences affect performance variables such as capacity, impedance, discharge rate capability, and charging rates. Deviations from expected surface area can
also indicate impurities or undesirable particle size for component manufacturers. BET surface area measurements are routinely used to evaluate the accessible surface area of battery components all the way down to very low surface area materials, even less than 0.01 m^2/g, and is measured using manometric or flow physisorption techniques.

1.2 Pore Size and Volume

The determination of pore volume and pore size is also of interest for battery materials. For example, changes in the pore size distribution of an electrode material could indicate phase transformations or structural changes in the material over the course of its practical use. These measurements can also be used to determine the correlation between a material's compression and annealing temperature and its resulting pore size distribution. Pore volume is also an important property. For example, in a battery separator this volume must be able to host a sufficient amount of liquid electrolyte for efficient ionic conductivity. Mercury intrusion porosimetry and gas sorption are routinely used to assess these properties.

The choice of technique is dictated by the pore size range within the material, with gas sorption being used for micropores (< 2 nm) and mesopores (2-50 nm) and mercury intrusion being used for large mesopores (> 5 nm) and macropores (> 50 nm).

1.2.1 Through-Pore Size and Permeability

For battery separators, the through-pore (pore that starts at one end and empties out the other) size distribution may be more important for a given application than a total pore size distribution. Characterization of the through pores can be done using capillary flow porometry. Permeability analyses can also be performed in order to get a sense of the structural nature of the pores. As an example, a tortuous pathway helps to isolate the positive electrode particles from the negative electrode material, but increases the effective resistance caused by the separator, thereby reducing battery efficiency and lifetime.

1.3 Density

Volumetric capacity is a crucial property of battery devices that operate in limited spaces. Understanding the volume occupied by the electrode material itself, as well as the open spaces within the matrix, often referred to as the material's porosity, is necessary for predicting performance.

Tapped density analyzers provide mass per volume information, including the spaces within and between particles, of the powders used to manufacture electrode components. Gas pycnometry is used to measure the true or skeletal density of a material and excludes the influence of any pores accessible from the exterior of the sample. For a regular shaped sample, where the dimensions can be measured, % porosity can be calculated directly from the gas pycnometry data. In the case of powders or irregular shaped samples, volume and density measurements from gas pycnometry are often combined with other techniques such as gas sorption or mercury intrusion, which can give total pore volume information, in order to determine the % porosity of a material.

2 Examples

2.1 Surface Area of Anode and Cathode

Graphite anode and $LiNiCoMnO_2$ cathode materials were characterized using N_2 at 77 K gas sorption measurements in the linear BET surface area range (P/P_0 = 0.05-0.3). The resulting BET surface area plots are shown in Figure 1 and calculations give a surface area of 2.5 m^2/g for the anode and 1.5 m^2/g for the cathode.

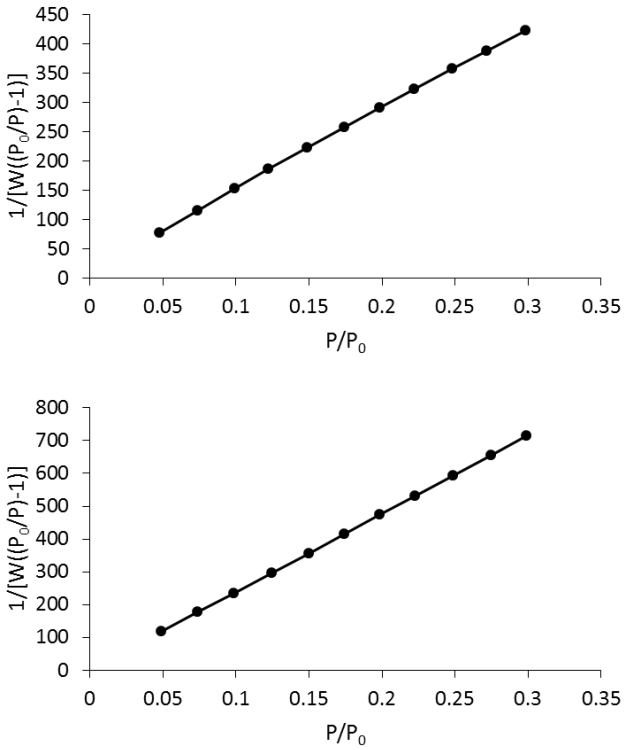


Figure 1: BET surface area plots derived from the N_2 (77 K) adsorption isotherms for graphite (anode, top) and $LiNiCoMnO_2$ (cathode, bottom) measured on a NovaTouch.

2.2 Surface Area and Pore Size of Separator

A battery separator comprised of polyvinylidine fluoride (PVDF) was characterized using mercury intrusion porosimetry for pore size and volume (Figure 2). The pore size distribution from mercury intrusion represents the distribution of all large meso- (2 to 50 nm) and macropores (> 50 nm) within the separator, regardless of whether they are through-pores are closed on one end (dead end). Porosity information can be obtained by combining the intruded pore volume from mercury with the skeletal density from helium pycnometry measurements.

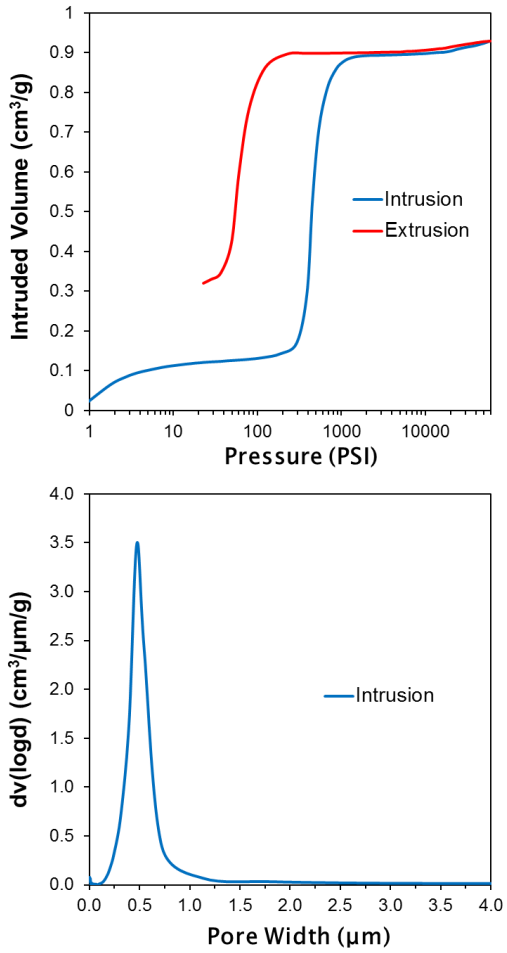


Figure 2: Mercury intrusion and extrusion curves measured on a PoreMaster 60 for PVDF separator (top) and its corresponding pore size distribution (bottom).

To determine which subset of the total pore size distribution are through-pores, porometry measurements were also performed on the separator (Figure 2). The mean pore size, 0.47 µm for both mercury intrusion and porometry, and pore size distributions from the two techniques was nearly comparable in this case, indicating this separator consists primarily of the desired and efficient through-pores.

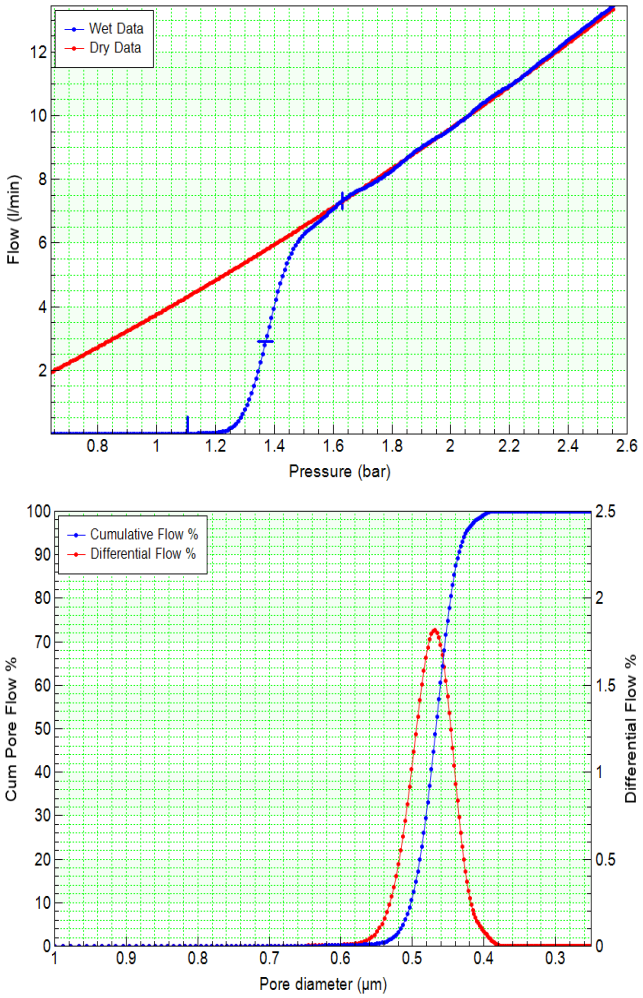


Figure 3: Capillary flow porometry curves measured on a Porometer 3Gzh for PVDF separator (top) and corresponding through pore size distribution (bottom).

2.3 Microporous Carbon Support for Li/S Battery

Not only can the anode, cathode, and separator materials be directly characterized by the techniques presented, but the supports in Li/S (or other types of) batteries can be characterized using gas sorption. In the case of a microporous carbon support, the pores may be sufficiently small (< 1 nm) to warrant the use of CO_2 adsorption at 273 K for pore size distribution calculation. Figure 4 shows a CO_2 (273 K) isotherm on a microporous carbon support and its corresponding NLDFT pore size distribution and cumulative pore volume. In this particular support, only pores smaller than 1 nm are present, with the majority smaller than 0.6 nm [1]. Consequently, only S_2 molecules can be confined in the pores and larger S_{4-8} molecules are excluded.

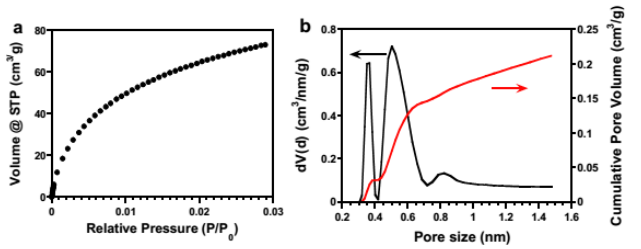


Figure 4: CO2 (273 K) adsorption isotherm measured on an Autosorb-iQ on microporous carbon Li/S battery support (left) and corresponding NLDFT pore size distribution and cumulative pore volume curves (right).

2.4 Supercapacitor

Supercapacitor materials, such as graphene and graphene oxides, can also be efficiently characterized using gas adsorption. In the example shown in Figure 5, an exfoliated graphene oxide was characterized by combining N_2 (77 K), Ar (87 K), and CO_2 (273 K) adsorption to calculate the complete micro- and mesopore size distribution [2]. In this example, N_2 and CO_2 gases are necessary to obtain the complete pore size distribution, as the material contains pores smaller than can be accessed by N_2, but also larger than can be accessed by CO_2.

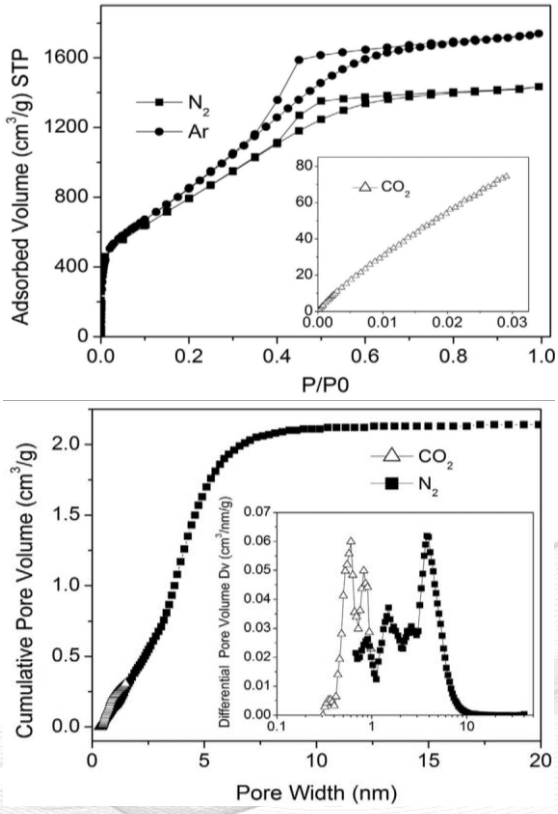


Figure 5: Adsorption isotherms measured on an Autosorb-iQ XR on graphene oxide super-capacitor (top) and corresponding pore size distributions (bottom).

3 Conclusions

The structural characterization of battery materials, including anodes, cathodes, separators, supports, and supercapacitors, can be accomplished by combining techniques such as gas adsorption (for BET surface area and micro- and mesopore size analyses), mercury intrusion (for meso- and macropore size determination), capillary flow porometry (for through-pore size distribution), and pycnometry (for density determination). Understanding these important physical properties of battery components can aid in future design and optimization, and help validate components in QA and QC environments.

4 References

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2. Zhu, Y.; Murali, S.; Stoller, M.D.; Ganesh, K.J.; Cai, W.; Ferreira, P.J.; Pirkle, A.; Wallace, R.M.; Cychosz, K.A.; Thommes, M.; Su, D.; Stach, E.A.; Ruoff, R.S. *Science* **2011**, *332*, 1537-1541.

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