COVALENT METROLOGY

Covalent Academy Episode 37 Q&A

Battery Material Quality: The Importance of Physical Properties

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01

Q: How would using Argon affect the BET measurement for a microporous material?

Answer: Because argon has no quadrupole (unlike nitrogen which does), and its boiling point is 10K higher than that of nitrogen, the micropore filling pressure is about two orders of magnitude higher than for nitrogen. This makes the measurement faster (typically twice as fast) and the resulting pore size results are more reliable as argon is much less sensitive to the polar nature of the surface as is nitrogen. Argon adsorption at liquid argon temperature is recommended by IUPAC.

02

Q: Since you've discussed some battery anode materials – particularly graphite and graphene – could you please also elaborate a bit on the uses and test cases of Fullerenes (C60 and C70) in anode or cathode materials? What specific tests would you recommend conducting on these materials?

Answer: I've no personal experience with fullerenes, however it is obvious that the structure of C60 and C70 are very different form the layer structure of graphite. It is the intercalation of lithium…

…ions between the graphene layers of graphite that gives high storage capacity and reversibility. I would not expect the same of fullerenes. Fullerenes however can provide electronic conductivity across their surface which could be superior to carbon blacks. I would draw your attention to this paper:

https://dds.sciengine.com/cfs/files/pdfs/2095-4956/01DBD6005A624ACF94ACD168577DA58A.pdf
"Fullerenes for rechargeable battery applications: Recent developments and future perspectives"
Zhipeng Jiang et al, Journal of Energy Chemistry, Volume 55, April 2021, Pages 70-79

03

Q: Have you previously used Pycnometry measurements to calculate the porosity of a material? How accurate is the porosity measurement when made this way?

Answer: Gas pycnometry provides the skeletal volume of the material, that is the volume of the solid phase plus any closed porosity. Skeletal density is calculated form this volume. The geometric or envelope volume of a "solid" includes the skeletal volume plus the volume of open pores. The difference between the two volumes (skeletal and geometric) gives the pore volume directly which, when expressed as a r=fraction or percentage of the geometric volume gives "porosity".

04

Q: What considerations apply when performing Pycnometry on coated electrodes?

Answer: Coated as in active material coated on a foil? If it's the density of the dried film coating you need, you have to take into account the volume of the foil. This can be calculated from its size (area and thickness) and hand-subtracted from the measured volume of the coated foil. Or coated, like a conformal coating, as in a separate process to coat the fabricated electrode? Gas pycnometry won't care about that, but obviously the volume of the coating will be included in the final measurement. Coatings can also block off open porosity rather than filling it, so the final density will be lower than the skeletal density of the individual components(ingredients).

05

Q: If you had a cathode electrode material known to absorb significant amounts of water, does this affect skeletal density measurement methods? Would you recommend removing all the water from the material prior to measuring skeletal density?

Answer: Yes, adsorbed moisture will affect the final results in two ways… the water has its own volume and density, plus it can express a vapor pressure (how much depends on how strongly…

…the moisture is adsorbed to the active material). The sample can be pre-dried in an oven and cooled in a desiccator. Rapid weighing should minimize moisture pickup. The instrument will purge the sample prior to analysis which will strip off any residual. This purge can be done as a series of pulses (pressurize/depressurize) of pure dry analysis gas, or timed flow (of pure dry analysis gas) or a timed evacuation period. In the limit, where moisture pickup is rapid and very significant, the whole unit can be placed in a glove box so a freshly prepared sample never sees ambient lab atmosphere.

06

Q: Are all these tools equipped with options for testing corrosion-resistant materials? Or, can analysis be completed on samples coated to improve their corrosion-resistance?

Answer: surface area and density measurements are all done dry, so its no problem to analyze coated materials… just beware of sample preparation, i.e. degassing, temperatures for surface area. Particle size can be done as a wet dispersion (so consider solubility of coating) or as a dry dispersion (using compressed air). Measurements like X-ray diffraction shouldn't care. Surface sensitive measurements like FTIR and Raman will be interesting methods in this context.

07

Q: How will the cathode and anode material bind together during dry coating, since no solvent is added?

Answer: This is done with addition of binders such as PRFE, which when mixed with powders with heat treatment, form a fibrous network that holds the entire mixture together … this open access paper should throw some light on the subject https://www.mdpi.com/1996-1944/17/10/2349 Kaiqi Zhang et al" Dry Electrode Processing Technology and Binders" Materials 2024, 17(10), 2349; https://doi.org/10.3390/ma17102349 Initial adhesion is through van der Waals forces, so particle size/surface area will play a role.

08

Q: For the dry-coating process, what will be some of the most important parameters to assess for the raw materials, given that no slurry is being prepared?

Answer: Powder rheology, particle size, surface area and density.

09

Q: Is it possible to assess the porosity of electrodes *after* coating?

Answer: Yes, open porosity can be investigated directly by, for example, mercury intrusion porosimetry (or if the pores are small enough by gas adsorption), or by comparing geometric volume (dimensions) with gas pycnometric volume. When closed porosity is present, it is evaluated by comparing geometric density (from dimensions) and theoretical skeletal density of the components (which could have been measured for each individual “ingredient” by gas pycnometry).

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