

“Thou Shalt Not Make Unto Thee Any Graven Image”: Some Remarks on X-ray Scattering and Materials Science.

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The science and technology of materials for energy storage and conversion in batteries, capacitors, fuel cells, solar cells and electrolyzers has been field of great interest for researchers for hundreds of years. The comprehension and control of the transport properties of such often electrochemical energy systems is essential for the function and integrity of the devices.

The transport properties in this context include the (i) electric charge transport, (ii) the mass transport, the (iii) heat and thermal transport and, (iv), the optical transport. The charge carriers for (i) include the electrons, electron holes, ions and more complex entities such as polarons, for example. The mass transport in (ii) includes fluids such as liquids and gases, and as these can be of ionic nature, this mass transport can be coupled with electric transport. When we are dealing with devices, Joule heat may involve and its control may be very critical for operation and integrity; this is a very complex topic of its own typically handled by the mechanical engineers. And whenever we deal with solar cells and photo electrochemical cells, the optical transport is considered.

All these transport properties depend on the “structure”. Structure, however, is a diffuse term. A microscopist has a different understanding of structure than a neutron scatterer, to name only these two. In my very own and admittedly poor definition, structure is something multi-dimensional which starts at the atomic scale and extends to the design of components and architecture of systems.

As 1) this conference is about microscopy and 2) I am not a microscopist, I have to span the arc from my own position and background to the scope of the conference. If we really want to do a good job as researchers, be it in microscopy, be it in scattering or any other scientific method, we do not only make a measurement but we also look at the potential consequences that arise from the data. Our work as researchers is therefore to a very large extent of analytical nature.

When we go back and look into the architecture of systems, we can rest conceptually on what architects do, and this is giving material a shape, a *form* which brings about a particular *function*. The relationship between form and function is well known to designers and architects. “Form and Function” was first coined by artist Horatio Greenough [1] in the 19th Century, as Editor Harold E. Small explains:

“Greenough was three generations ahead of his time. ... It was Greenough, not Whitman, who first protested against meaningless ornamentation. It was Greenough, not Ruskin, who first expressed the idea that the buildings and art of a people express their morality. It was Greenough, not Le Corbusier, who first said that buildings de-signed primarily for use "may be called machines." It was Greenough, not Louis Sullivan, who first enunciated the principle that, in architecture, form must follow function.”

The aforementioned generalizations made by Greenough are noteworthy for what we researchers do in our field. Let me therefore identify the term “form” with structure, which mandates the function. In our structure analyses we seek to identify those objects which are components that assemble up to “machines”, as we know from Le Corbusier. Objects with function are the organs which make machines.

It was the Bauhaus half a century later whose philosophy rejected all ornaments so that form was left with function only. This reductionist philosophy is widely essential to our scientific method, particularly in physics which aims at reducing everything into systems with high symmetry. Unintentionally we mistake that we end up with less and lesser function, because function is a result of complexity and not simplicity, as Anderson [2] explains in his paper on interdisciplinarity and complexity.

It is possibly because of the complexity of our vision apparatus that we prefer the visuals of microscopy data over almost any other form of data. Let me therefore begin with an example from biology where the “Bauplan” of the photosynthetic apparatus – an energy storage and conversion device - has been elucidated progressively by microscopy methods. The naked eye sees structures in the leaf of plants which become visible as cells in the spyglass and microscope. We can even identify the chloroplasts with an optical microscope, provided we do the necessary “sample prep”. It requires further “sample prep” when we want to resolve the thylakoids in the chloroplasts with an electron microscope.

Considerable improvement was made with the combination of electron microscopy with energy dispersive x-ray (EDX) spectroscopy, because we gain now images with high spatial resolution and element specificity. The electron energy loss spectroscopy (EELS) which is nowadays available with transmission electron microscopes (TEM) permits to some extent the resolution of the electronic structure (or molecular structure) of materials with resolution virtually at the atomic scale.

As we zoom further into the photosynthetic apparatus, we find the thylakoids with the thylakoid membrane and the photosystems, which include the light harvesting complexes and the reaction centers. I have not come across a microscopy visualization of these yet. The metalloproteins such as oxygenase and hydrogenase have metal centers which are bridged with ligand groups, i.e. Mn-O-O-Mn and Fe-S-S-Fe/Ni. Their molecular scale structure cannot be resolved with microscopy.

This is why protein crystallography (PX) was developed – with much success – by taking advantage of the anomalous dispersion of x-rays. Multi-anomalous diffraction (MAD) phasing brings about the element specificity with high accuracy in protein crystallography [3] and in crystallography in general.

Not all relevant issues at the molecular can be addressed with diffraction. The charge transfer across the aforementioned Mn-O-Mn and Fe-S-Fe superexchange units in proteins follows the Goodenough-Kanamori rules [4] the same way like the corresponding structures in lithium ion battery positive electrodes and solid oxide fuel cell cathodes. The spin of the ions determines whether electrons can hop across the unit, or not. This is why K- β spectroscopy or L-edge NEXAFS spectroscopy, methods very sensitive to the spin structure, are used for analyses of such systems. But here no atomic resolution is available yet. Notwithstanding that methods like X-PEEM and STXM allow for high quality electronic and molecular structure determination with spatial resolution down to 30 nm.

The bond length, spin state, oxidation state and hybridization effects determine to a large extent the electric transport, which can be elucidated with the aforementioned hard and soft (and tender) x-ray

spectroscopy methods. But problems still persist. For example, the hydrogenase co-factors are accompanied by an iron-sulfur cluster which spectroscopically cannot be distinguished from the iron-sulfur co-factor. This is why typically the nickel hydrogenases and not the iron hydrogenases are studied with x-ray spectroscopy.

If there was a chance to probe the hydrogenase locally with x-ray spectroscopy, we would maybe be able to tell the difference in operation of a nickel hydrogenase from a sulfur hydrogenase, if there was any difference. Local probes are therefore necessary for the further discrimination of structures in a larger assembly of materials with different structure and morphology, such as electrode assemblies.

There are cases where we can probe deeper into complex structures by taking advantage of the penetration depth of x-rays and electrons. X-ray interferometry, reflectometry and grating-angle methods allow for probing flat and laminar structures with depth sensitivity in the nanometer range [5]. The penetration depth of x-rays allows therefore to some extent for *in situ* and, more interesting, for *operando* experiments where the materials in a component or complete device is probed non-destructive with x-rays while at the same time, for example, electroanalytical methods can be employed.

This approach can permit a parameterization of device settings and corresponding structure changes which in the ideal case can be mathematically modelled to the extent that the relationship of “form and function” is fully recovered at the quantitative level.

Not only the atomic scale but also the mesoscale can be relevant for function. In electrochemistry this can be for example nanoparticle electrocatalysts or the high internal surface area of porous electrodes. Small angle scattering is the method of choice for probing this size range and correlate it for example with the ionic conductivity. An example from photosynthesis is the conformational changes in the *bacteriorhodopsin* proton pump: small angle scattering with neutrons maps the conformational changes at the mesoscale, and quasi-elastic neutron scattering produces the proton conductivity [6], but with no real space images.

We are therefore still left in the position that we have to “imagine” the structure of devices and systems based on their function, unless we can map all details at all relevant scales in the real space.

References:

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