



## ADVANCED MATERIALS SCIENCE

Fields of Expertise TU Graz

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**Anna Maria Coclite,  
Christof Sommitsch,  
Gregor Trimmel**  
**Advanced Materials Science**

Source: Lunghammer – TU Graz

We are happy to announce that the Field of Expertise Advanced Material Science has a new management team: Anna Maria Coclite from the Institute of Solid State Physics, Christof Sommitsch from the Institute of Material Science, Joining and Forming and Gregor

Trimmel from the Institute for Chemistry and Technology of Materials.

Anna Maria Coclite works on surface modification by thin film deposition. A thin film is a layer of material ranging from fractions of a nanometer to several micrometers in thickness. The future generation of devices, e.g. wearable electronics, requires miniaturization and control of the material properties to the nanoscale. For this reason, advanced methods for the growth of thin films are being studied in Anna's lab. She also received an ERC Starting grant of approx. 1.5 million euros to combine different thin films and form a sensor matrix for applications as artificial skins.

Christof Sommitsch is focusing on the development of new structural materials such as ultra-high strength steels and high-temperature materials. Differ-

ent additive manufacturing processes i.e. wire and powderbed-based printing are investigated. For the latter, selective laser melting of Ti alloys, tool steels and magnetic materials are studied. In addition, material design and manufacturing is supported by physically based modeling and simulation. Materials behaviour during thermo-mechanical processing (forming, joining) and in service (creep, corrosion) is tested and analysed by means of advanced lab equipment.

Gregor Trimmel looks at new materials for photovoltaics with a special focus on the preparation of new organic semiconductors, lead-free perovskites as well as inorganic-organic hybrid systems for alternative, printable and flexible solar cells. In addition, he works on the synthesis of functional polymers and the development of elastomeric materials.

### **Bernhard Gadermaier:**

## **Extending the Building Blocks of Materials Science: What Viruses have to Offer.**

When it comes to nanotechnology, nature is truly the most successful researcher. Whereas we are still struggling with large-scale production of three-dimensional, nano-sized materials, nature perfected this task in viruses long before the dawn of humanity. Bionanotechnologists use these viral structures as templates for the synthesis of nanostructured inorganic materials with new outstanding properties.

One of the major challenges of the 21st century is the need for sustainable energy conversion and energy storage devices. Therefore, we have to identify novel materials for energy storage and at the same time, we have to develop low-energy consuming and sustainable strategies to prepare such materials on a large scale. The use of biological templates represents an elegant way to alter the morphology and

properties of materials synthesized by e.g. aqueous precipitation routes. Using this approach, we prepared highly anisotropic cathode materials for Li-ion batteries with surface-dominated properties and particle shapes resembling the template. Such cathode materials are often amorphous, a state not easily attainable by other synthesis routes. The material properties of the amorphous state

are very different from those of their crystalline counterparts and are, if the particles are nano-sized, highly dependent on the shape, i.e. morphology, and concomitantly, on the surface-effects. Thus, the material properties can be changed and ultimately fine-tuned using this fairly novel and unconventional method. >

## BIOTEMLATION

There is plenty of space on the surface of a virus. We use the bacteriophage M13, a virus which exclusively infects *Escherichia coli*, as a biological template for the synthesis of iron phosphate nanowires. Iron phosphate ( $\text{FePO}_4$ ) is a very promising active material used in battery cathodes. This material offers high-charge storage capacities and is very eco-friendly, consisting of highly abundant elements. However, it has certain drawbacks such as low electronic and Li-ionic conductivities – two quantities that essentially define the performance of cathode materials. Currently, this material is used in batteries but requires an energy-demanding synthesis route which yields micro- to nano-sized carbon coated  $\text{LiFePO}_4$ , which is the discharge product of  $\text{FePO}_4$ . Increasing the surface-to-volume ratio significantly reduces diffusion lengths [1], [2] and increases performance, whereas carbon-coating enables efficient electronic transport thereby enabling fast redox reactions to occur. Nevertheless, for crystalline  $(\text{Li})\text{FePO}_4$ , a classic example of a two-phase material [3], the crystallinity grants an almost constant poten-

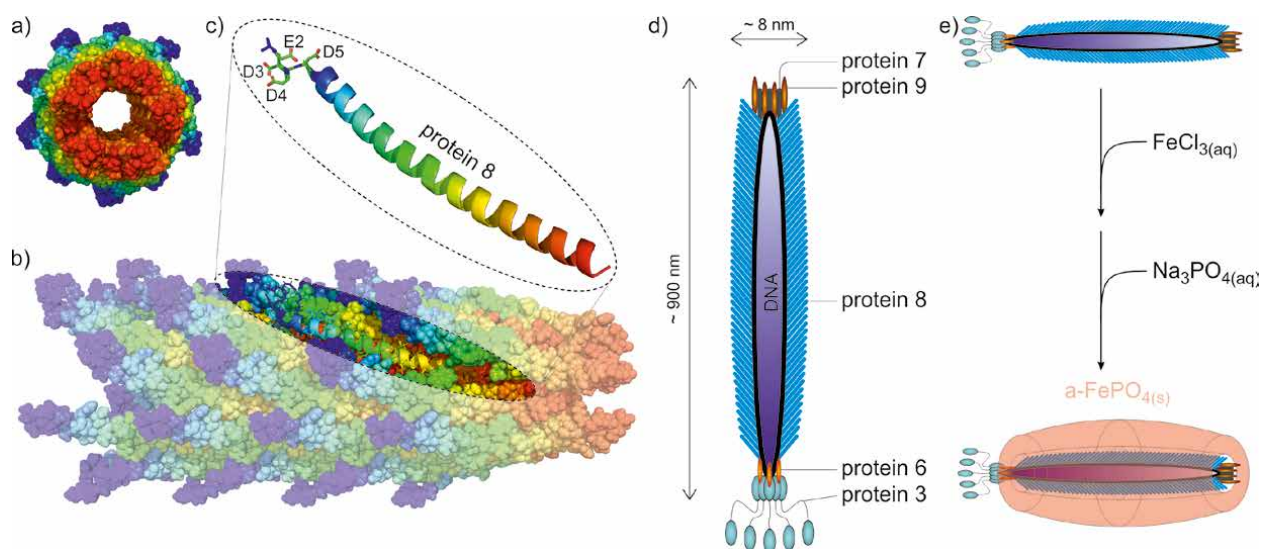
tial during charge/discharge but also restricts Li-ion diffusion to one-dimensional (1D) channels that are easily blocked by defects. For amorphous  $(\text{Li})\text{FePO}_4$  the situation might be very different, and the Li-ion conductivity is anticipated to be much higher as the ionic transport is no longer restricted to 1D-channels.

The filamentous bacteriophage M13 can easily be genetically engineered to harbour specific properties. Most importantly, thousands of copies of protein 8 foremost assemble its proteinaceous coat (capsid). Thus, by genetically modifying the genetic code for protein 8, we can easily control the surface properties of the bacteriophage as these properties depend on the specific surface-exposed amino acids. To use this bacteriophage for our synthesis, we mutated the genetic information coding for protein 8 so that it would carry four acidic amino acids at its N-terminal tail (Figure 1a blue regions). These surface-protruding regions show a pattern of four consecutive acidic amino acids, namely glutamic acid (E) followed by three residues of aspartic acid (D), which enables the surface of the bacteriophage to electrostatically bind cations.

## GREEN SYNTHESIS OF CATHODE MATERIALS

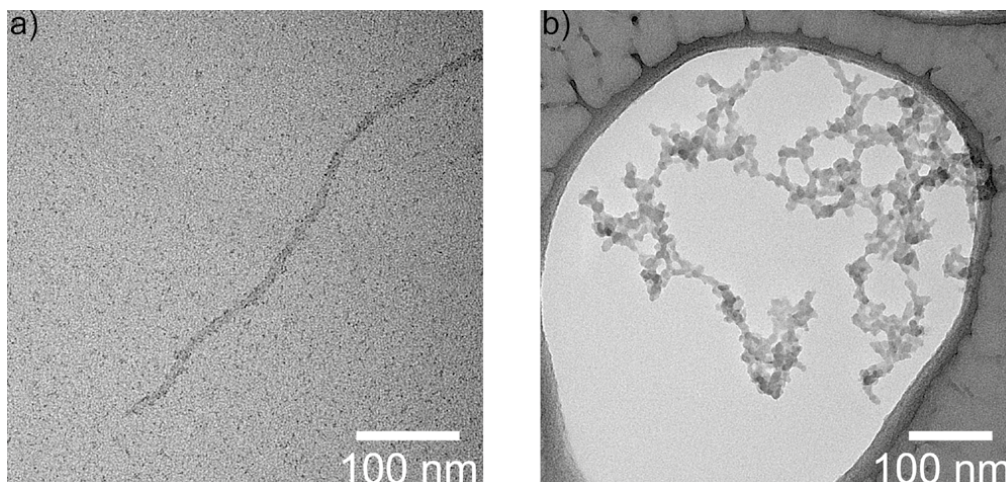
Here we used the modified bacteriophage M13 as a template for the synthesis of the charged cathode material  $\text{FePO}_4$ . In a simple aqueous synthesis process the bacteriophage is first incubated with an  $\text{Fe}^{3+}$  containing solution to allow its surface to coordinate sufficient iron cations (Figure 2a).

In a subsequent step, the addition of a  $\text{PO}_4^{3-}$  containing solution leads to the rapid precipitation of amorphous  $\text{FePO}_4$  due to its very low solubility product. Most importantly, the precipitates adopt the filamentous form of the template resulting in entangled nanowires of amorphous  $\text{FePO}_4$  (Figure 2b). In this manner, amorphous  $\text{FePO}_4$  nanowires can be synthesized by employing a biotemplated aqueous precipitation route at room temperature. Without the restrictions imposed by the crystal structure of  $\text{LiFePO}_4$ , the Li-ion conductivity is much higher. Purification by filtration and subsequent drying at comparatively low temperatures renders this material ready to use for Li-ion batteries.



**Figure 1: Capsid model of the bacteriophage M13 [4]-[5]. Top-view (a) and side view (b). The modified protein 8 containing the acidic N-terminus is shown in (c). Schematics of the bacteriophage M13 (d) and a simplified flow chart of the green synthesis of amorphous iron phosphate nanowires (e).**

Source: Institute for Chemistry and Technology of Materials.



**Figure 2: Transmission electron microscopy images of the modified bacteriophage M13 after incubation in iron chloride solution (a) and after subsequent precipitation as amorphous  $\text{FePO}_4$  nanowires (b).**

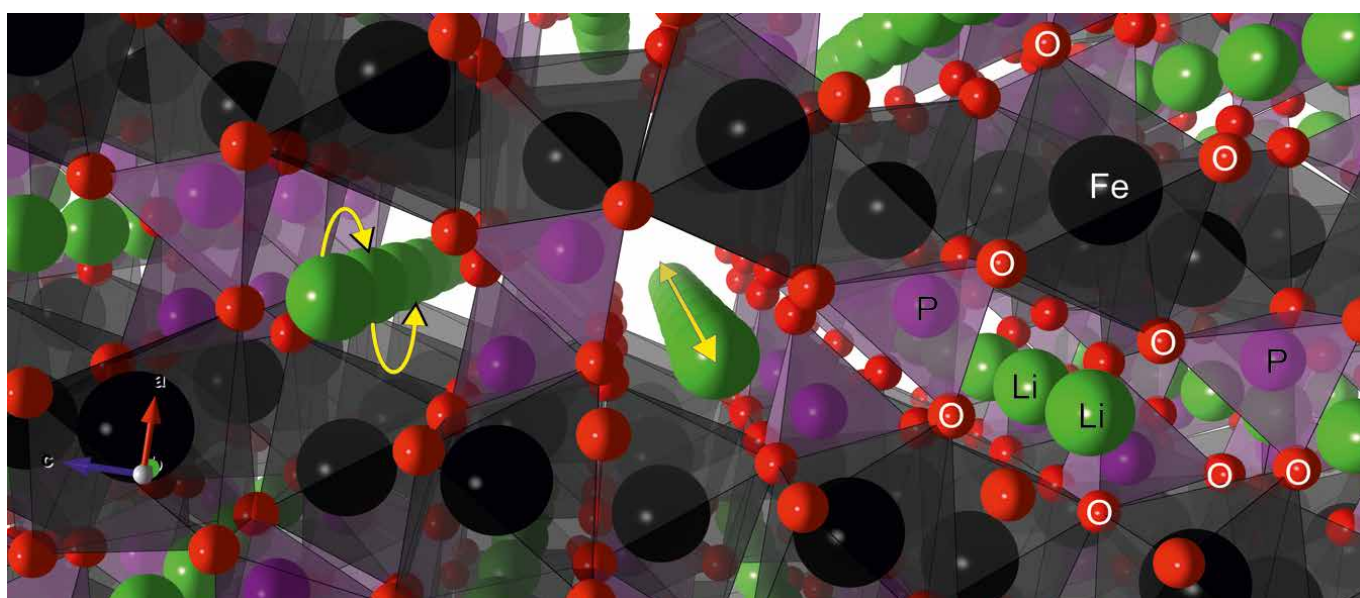
Source: Institute for Chemistry and Technology of Materials.

## PERFORMANCE

Li-ion cells with cathodes of  $\text{a-LiFePO}_4$  offer a great advantage compared to cells using its crystalline counterpart. As the potential of this cathode highly depends on the state of charge, which is the amount of Li stored in the cathode material, for this type of cells the state of charge (SOC) can be determined easily. In  $\text{c-LiFePO}_4$  with its very flat plateau, estimation of the SOC is difficult, especially if the cell is not at rest, i.e., if the cell is delivering power.

As intimated above, the diffusion of Li-ions is highly influenced by the crystal structure of  $\text{LiFePO}_4$ , which allows the ions to diffuse almost exclusively within the one-dimensional channels (Figure 3). If the long-range order of the atoms within the material is abolished, so are the restrictions imposed by the arrangements, and the Li-ions are facing a surrounding with a less restrictive degree of freedom i.e. 3D diffusion is rendered possible. Many cathode materials suffer from

structural disorder; however, this is not the case for  $\text{LiFePO}_4$ . It is well known that disorder and vacancies can increase conductivity by several orders of magnitude and amorphous  $\text{LiFePO}_4$  is one of the very few cathode materials for which this holds. Without the restrictions imposed by the crystal structure of  $\text{LiFePO}_4$ , the Li-ion conductivity is much higher. Tests of chemically lithiated  $\text{a-FePO}_4$  ( $\text{a-LiFePO}_4$ ) by impedance spectroscopy clearly show the outstanding increase >



**Figure 3: Crystal structure of lithium iron phosphate,  $\text{LiFePO}_4$ . The octahedrally coordinated Fe-ions (black) form a sheet connected by tetrahedrally coordinated P (purple). Lithium ions (green) preferentially move within the formed 1-dimensional channels by jump processes (yellow arrows).**

Source: Institute for Chemistry and Technology of Materials.

of the conductivity,  $\sigma_{DC}$ , compared to its crystalline counterparts; even so if the crystallites are nanosized (Figure 4). The ionic conductivity shows a typical increase with temperature and can be well described by the famous Arrhenius relation. Close to room temperature, the conductivity of the biotemplated amorphous  $\text{LiFePO}_4$  is increased by almost three orders of magnitude even compared to crystalline  $\text{LiFePO}_4$  with particle sizes of 50 nm. Interestingly, the activation energies associated with the mean energy barrier ions have to overcome in order to diffuse are significantly reduced from  $\sim 0.6$  eV to  $\sim 0.36$  eV, which corroborates well with theory.

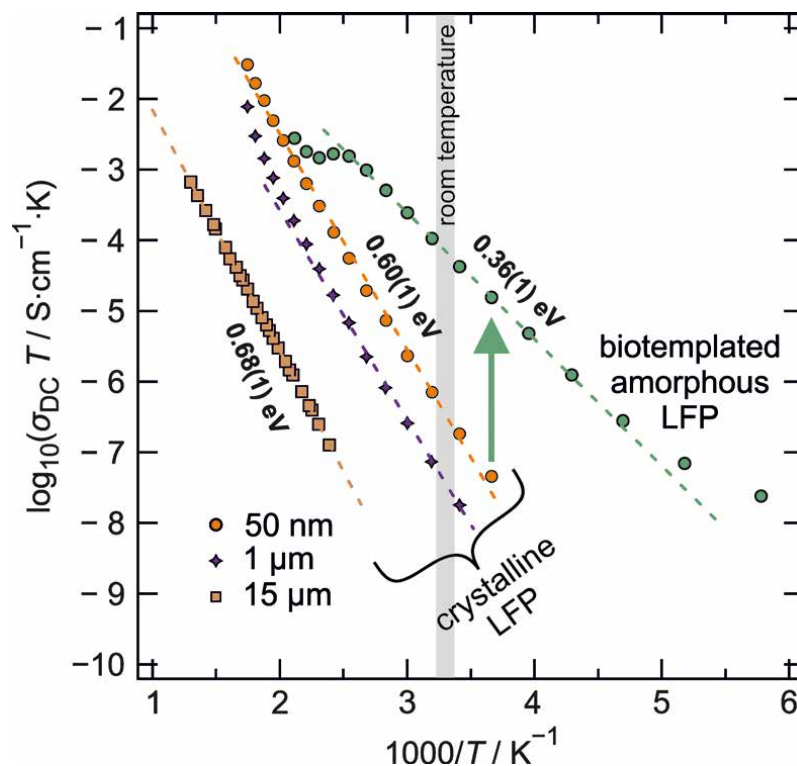
**Figure 4: Temperature dependent conductivity,  $\sigma_{DC} \cdot T$ , of crystalline  $\text{LiFePO}_4$  and biotemplated amorphous  $\text{LiFePO}_4$  as a function of the inverse temperature in an Arrhenius representation. Clearly, the activation barrier for conduction is significantly decreased in a-LFP (0.36 eV) compared to c-LFP (0.6–0.7 eV)<sup>6,7</sup> whereas the conductivity at room temperature is increased by three orders of magnitude.**

Source: Institute for Chemistry and Technology of Materials.

## OUTLOOK

The use of viruses as building blocks in materials science extends the possibilities of fine-tuning material properties by shaping nanosized materials. With the synthesis of amorphous  $\text{FePO}_4$  nanowires we are just scratching at the surface of what is possible with these templates. With this tool at hand, the synthesis of nanocomposite materials is just one step away from the synthesis of isotropic nanomaterials. The tips of the bacteriophage M13 composed by either protein 7 & 9 or 6 & 3 can also be altered in a way to have specific binding capabilities for various materials. Using these additional modification attributes, the formation of 3D organized nano scaffolds will be possible.

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**Bernhard Gadermaier is a PhD student at the Institute for Chemistry and Technology of Materials where he is carrying out his thesis in the group of Martin Wilkening.**

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