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ADVANCED MATERIALS SCIENCE

Fields of Expertise TU Graz

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Source: Lunghammer – TU Graz

Covid-19 has not limited the productivity and creativity of the Field of Expertise Advanced Materials Science. Although still restricted in our daily laboratory work, many of our members have used the time working from home to write scientific papers or apply for research funds. In the 14th call of the initial seed funding programme of TU Graz, we were able to finance four interesting project ideas in chemistry, physics, mechanical engineering and electrical engineering. The awardees were Andreas Drexler with a project on hydrogen embrittlement of dual-phase steels, Ilie Hanzu working on in-operando characterization methods of ion transport in solids, Annette Mütze with an interdisciplinary project idea on laser cutting technologies, and Matiss Reinfelds on a new class of organic semiconductors for solar cells. We wish them good luck for the proposal submission, and we look forward to your submissions for the next call.

In order to foster networking of the Field of Expertise despite the Covid-19 pandemic, we carried out the FoE AMS *update* for the first time to inform our members about the latest news within the Field of Expertise, to discuss current topics and to present exciting research projects. In the first edition, Birgitta Schultze-Bernhardt presented her ERC-starting grant project ELFIS – Electronic Fingerprint Spectroscopy and Gerald Kothleitner the project ANGSTROM – A Next Generation Scanning Transmission electROn Microscope for multidimensional imaging and fast spectroscopy within the FFG infrastructure call. The FoE AMS *update* will be held four times a year, online or in person, depending on the Covid-19 situation.

Finally, Qamar Abbas, Christian Prehal and their coworkers have gained interesting new insights regarding the persistent and reversible solid iodine electrodeposition in nanoporous carbons, which was recently published in Nature Communications and will be the topic of the next few pages. This is another example of vivid research activities within the Field of Expertise on energy materials.

Qamar Abbas:

A Sprinter that Runs on Water: Energy Storage with Hybrid Supercapacitors

Peak power demand puts a lot of pressure on primary electricity sources (grid or off-grid renewables) as well as on electrical equipment. Supercapacitors are the perfect solution for peak power saving as they deliver bursts of energy and then quickly capture excess power that is otherwise lost. Water-based supercapacitors can serve this purpose at low cost per kWh. >

Qamar Abbas obtained his PhD (Dr. techn.) from the Graz University of Technology and completed his habilitation at the Poznan University of Technology, Poland in 2018. Currently, he is a Lise Meitner fellow with Bernhard Gollas at the ICTM and his research is focused on supercapacitors and hybrid energy storage devices.

Source: Qamar Abbas

Among various electrical energy storage devices for industrial and electric grid applications, supercapacitors are the most promising ones owing to their high pulse power, rapid charge/discharge (in milliseconds), high efficiency and extremely long cycle life [1]. At the heart of this fast charge storage is porous activated carbon as electrode material with a surface area up to 2,000 $m^2 g^{-1}$. High specific surface >

area coupled with good intra- and interparticle conductivity in porous matrices gives accessibility of the liquid electrolyte to the pores (below 2 nm) of the carbon electrode. These carbons mainly consist of sp2 hybridized carbon atoms possessing mainly a honeycomb-like six-membered ring structure, which is bent by five- and seven-membered rings [2]. However, commercial capacitors utilize flammable, expensive organic electrolytes and tedious construction processes to achieve high energy values, which adds to the cost per kWh. Aqueous electrolytes, on the contrary, are highly conductive, eco-friendly and cheaply available, enabling supercapacitors to be safe, low cost and fast.

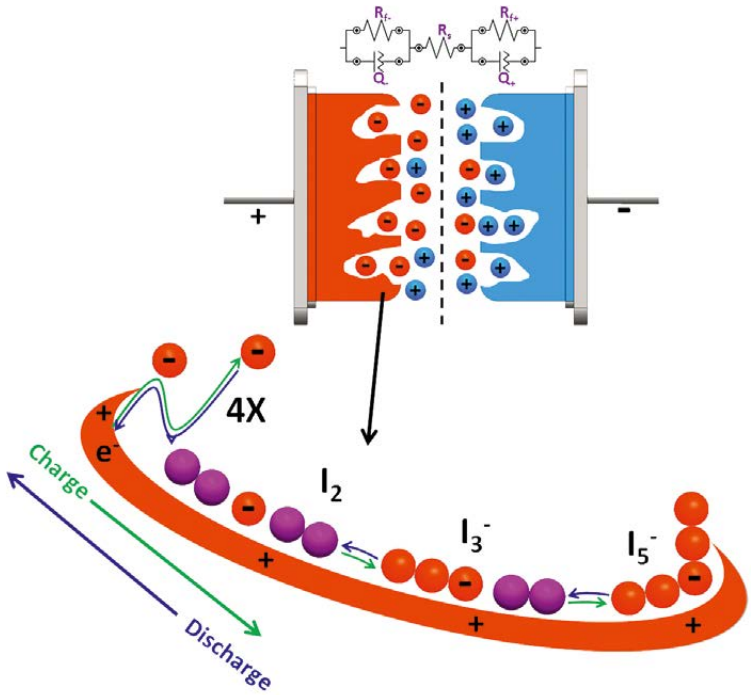
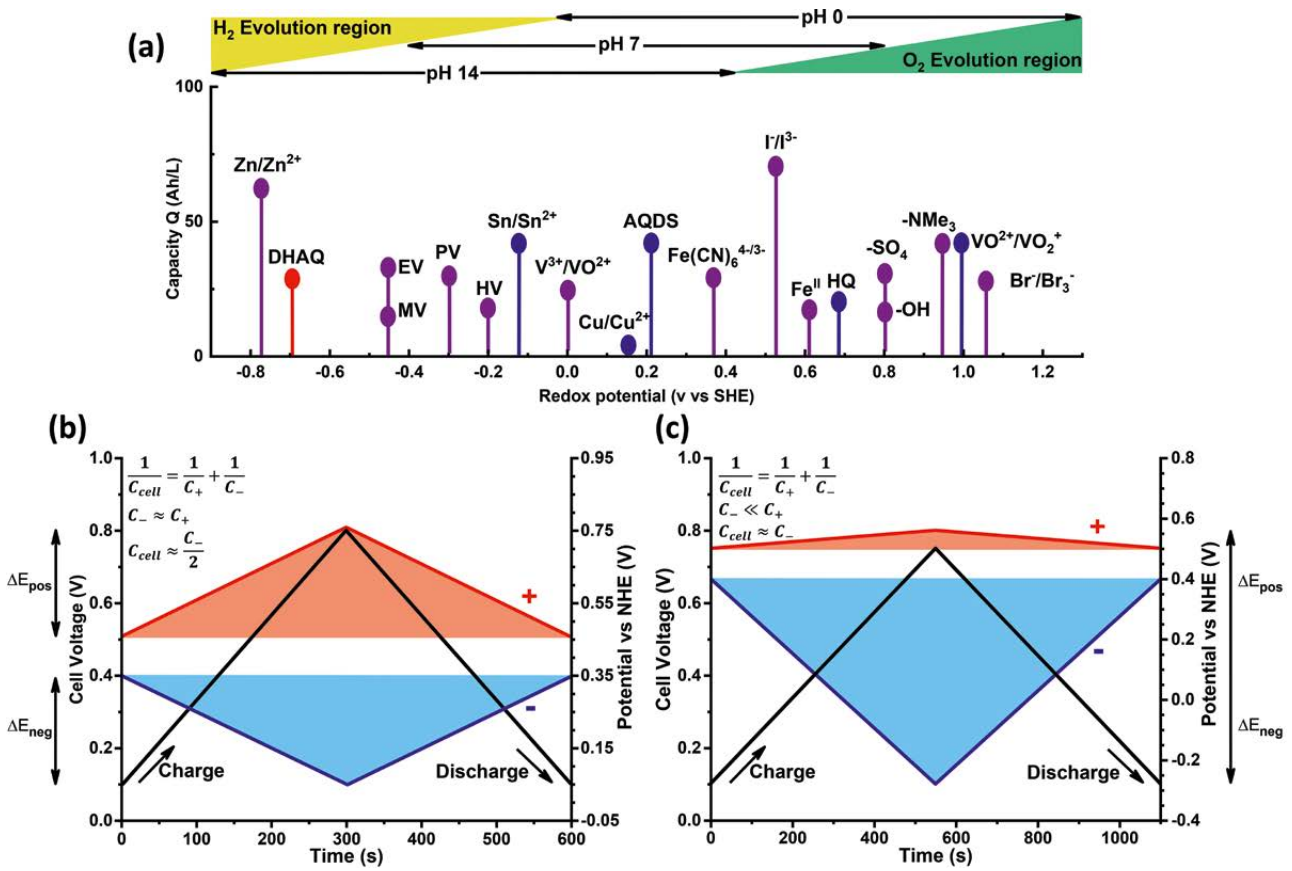


Figure 1: Schematic diagram of a charged hybrid supercapacitor in aqueous iodide-based electrolyte and corresponding equivalent circuit, R is resistor, Q is capacity (upper panel), oxidation of iodide to iodine in a pore and subsequent formation of polyiodides (lower panel).

Source: TU Graz / Institute for Chemistry and Technology of Materials / ICTM

Figure 2: Activity as a function of pH for various redox species (a) and distribution of potential windows in symmetric and hybrid supercapacitors (b-c).

Source: TU Graz / Institute for Chemistry and Technology of Materials / ICTM



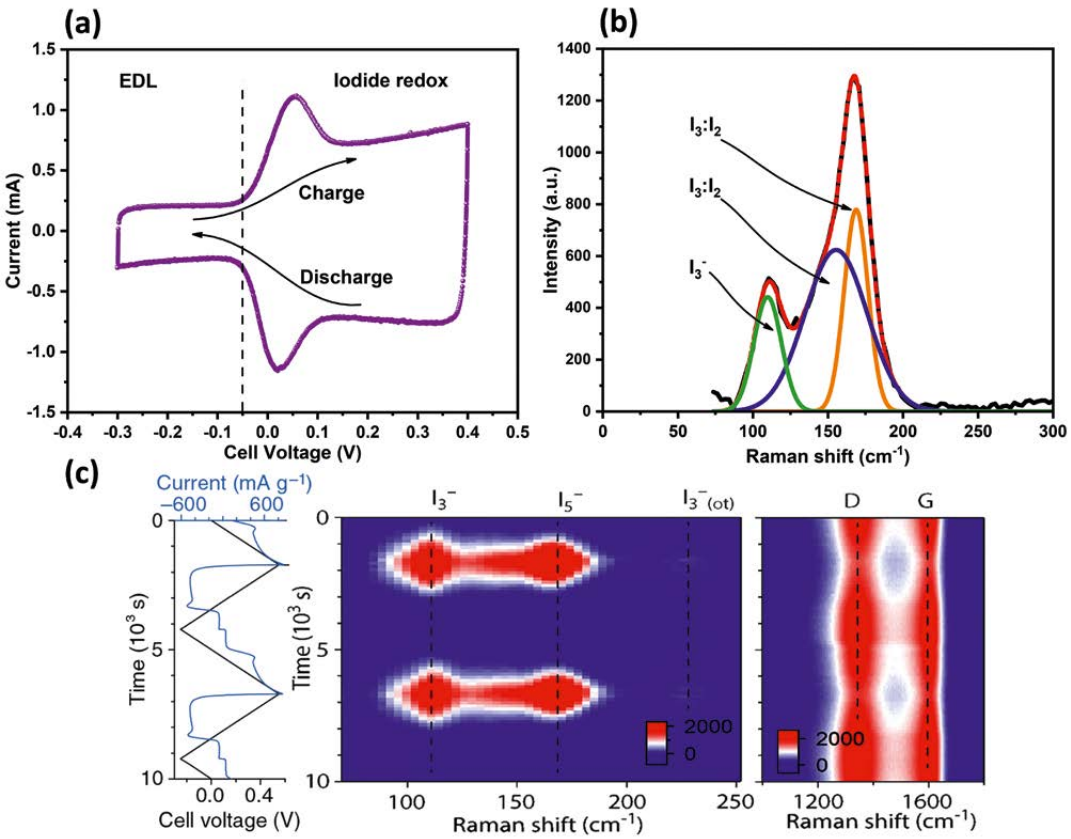


Figure 3: Cyclic voltammogram (a) and polyiodide Raman spectra of carbon electrode in iodide electrolyte (b), evolution of iodides, D- and G-band during in situ Raman investigation (c).

Source: TU Graz / Institute for Chemistry and Technology of Materials / ICTM

Hybrid supercapacitors with aqueous electrolytes are a new variant in the capacitive energy storage field whose performance matches that of organic-based supercapacitors [3]. They are constructed by coupling a capacitor electrode with a battery-like electrode in a single device. The capacitive charge storage mechanism in the electrochemical double layer (EDL) is permeation-selective cation adsorption at the negative electrode and ion-exchange at the positive electrode [4]. By replacing the positive EDL electrode with a battery electrode, the dominant charge storage mechanism becomes faradaic (redox reaction) at this polarity, while it retains perm-selective adsorption of cations at the negative electrode. In aqueous-based hybrid supercapacitors, a battery electrode based on the redox reaction of iodide ions in the electrolyte can be used. Iodide oxidation leads to the highly reversible electrodeposition of iodine in the nanopores of the carbon electrode, making it an efficient solid redox electrode. In contrast to a symmetric supercapacitor where both electrodes operate in nearly similar potential windows, the positive electrode in a hybrid supercapacitor possesses very narrow potential range because of its high redox capacity. Consequently, the negative electrode works in an enlarged potential window and storing charge in the EDL. Theoretically, double the amount of charge can be stored in a hybrid supercapacitor compared to its symmetric counterpart ($Q_{hybrid} = 2 \cdot Q_{symmetric}$) [5]. Various redox species can be used in aqueous electrolytes, but iodides are among the most stable and cheap, and possess highly reversible redox properties, suitable for fast charge/discharge.

In situ Raman spectroscopy has been used to track the charging mechanism of the iodine-carbon battery electrode in aqueous electrolyte. It monitors the evolution of triiodides (I_3^-) and pentaiodides (I_5^-) under solid-liquid conversion, indirectly proving that iodine is electrodeposited and stored in the carbon nanopores and then interacts with freely available I- ions to form polyiodides. Iodine interaction with the carbon electrode is also monitored in terms of carbon lattice parameters. Shifts in D- and G-band positions in combination with band width changes indicate a certain degree of charge transfer between carbon and iodine. During the charging step, an increasing amount of iodine is produced, which results in high charge transfer as indicated by a blue-shift of the D-band and a red-shift of the G-band. Small angle X-ray scattering >

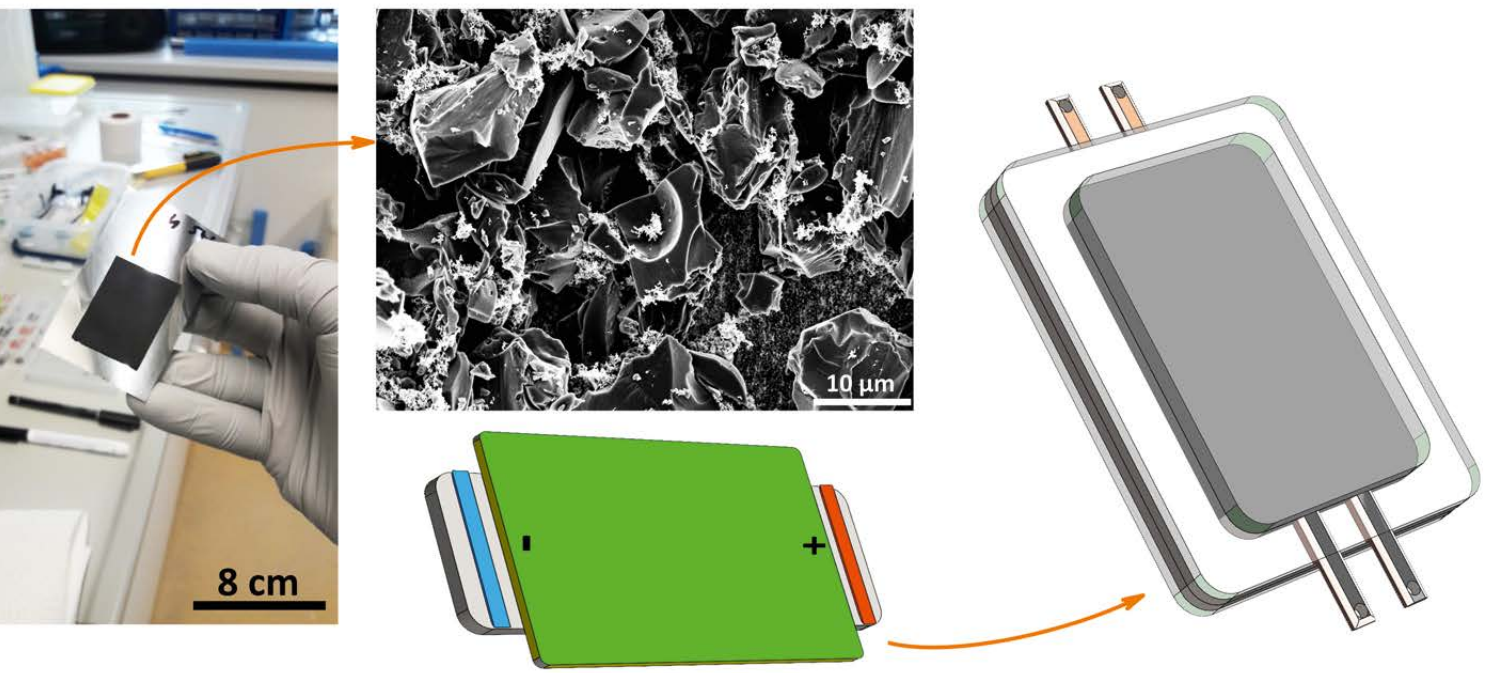


Figure 4:
Schematic diagram of a pouch cell construction.
Source: TU Graz / Institute for Chemistry and Technology of Materials / ICTM

provides direct proof of solid iodine electrodeposition in the carbon nanopores. Stable discharge capacities in the range of 150-160 mAh g^{-1} have been achieved via packing of electrodeposited iodine in the porosity of the carbon electrode and using neutral aqueous supporting electrolyte to block polyiodides shuttling [6].

Publication of this fundamentally interesting and highly promising behaviour has gained the interest of industrial partners. Currently, the laboratory knowledge about such hybrid supercapacitors is being transferred to prototype scale, where devices in the form of pouch cells are being realized. For this purpose, electrode material is prepared by using suitable proportions of activated carbon binder to integrate carbon particles and conductivity enhancer to improve charge propagation in the electrode matrix. Carbon particles and the current collector surface contacts are carefully monitored with electron microscopy and other surface-sensitive techniques. A layer of electrode material is applied onto the pre-treated current collector, calendared at room temperature and dried at 100 °C. Separator soaked in redox-active iodide-based electrolyte is placed between two electrodes and sealed under reduced pressure to exclude air. Our group at the Institute for Chemistry and Technology of Materials (ICTM) is capable of fabricating and testing such pouch cells. The performance of these hybrid supercapacitors is benchmarked against commercial state-of-the-art devices in a temperature range between -40°C and +60 °C.

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