Insecurity of power supplies and pollution of air and environment in mega-cities and industrial regions are among the greatest problems for mankind at the moment and ways out of these problems need to be found within only a few decades. Estonia, being a member of the European Union, has and will have serious problems connected with the fulfilling of the EU regulations, connected with the energetically ineffective chemical and oil-shale industry and exploitation of the thermo-mechanical cycle based technology to produce electricity in the North-Eastern part of Estonia in the near future. Taking into account the very low upper heating value for oil-shale, there are no elegant solutions based on the old historical thermodynamically limited electricity production conception applied in AS Eesti Energia. In addition, the residual heat as co-product of electricity cannot be used effectively as there is only one town, Narva, located at a reasonable distance from Baltic Thermal Power Station. There is no doubt that low and high temperature fuel cells, high temperature proton conductive electrolyzers and synthetic fuel synthesis reactors (where electricity, CO₂ and H₂O are used based on the designed nano/microstructural materials combined with wind turbines for hybrid energy storage/generation complexes) will be the most perspective “green” energy systems in the future for Estonia (Scheme 1). Therefore in the Chair of Physical Chemistry a lot of attention is paid for the development of micro-meso-porous materials for modern energy conversion and storage devices. Chair of Physical Chemistry is participating also in the development of The Estonian Energy Economy Development Plan 2014-2020.

Scheme 1. “Green” energy system.

**Low and medium temperature solid oxide fuel cells**

The chemical energy conversion efficiency increases with the rise in working temperature of FC, and for medium temperature solid oxide fuel cells (MT SOFC) (600 °C < T < 800 °C) [1-15] it is higher than 60-70%, compared with that for low temperature polymer electrolyte membrane fuel cells
(PEMFC) (~35-49%) [16-18]. Differently from PEMFC, where very clean hydrogen is indispensible, the MT SOFC are attractive energy conversion systems as various hydrogen containing compounds (natural gas, diesel and biodiesel, alkanes (gasoline), alcohols, esters, H2S, NH3, etc.) can be used as fuels. However, an important disadvantage of MT SOFC is the extremely quick electrochemical degradation of anodes and cathodes and also high temperature corrosion of current collectors and other construction elements. For MT SOFC Sm2O3-doped CeO2 (CSO), Gd2O3-doped CeO2 (CGO) or Sc2O3 stabilized ZrO2 (ZSO) can be used as electrolytes (G. Nurk, I. Kivi, P. Møller, M. Vestli, et al.). The MT SOFC anode is usually made from Ni/CSO cermets [1-14], however, some Ni-free anodes are being studied in the University of Tartu (K. Tamm, R. Küngas et al.) [13]. Unfortunately the rate of electroreduction of oxygen from air is a very slow process on the traditional cathode material La1-xSr2MnO3-δ (LSMO). One possibility to increase the catalytic activity is to use the electrochemically more active La1-xSr2CoO3-δ (LSCO), Pr1-xSr2CoO3-δ (PSCO), Gd1-xSr2CoO3-δ (GSCO) or La1-xSr2Co1-yFe2yO3-δ (LSCFO) cathodes [1-10], where x is the molar ratio of Sr2+ ions and y is the molar ratio of Fe3+ ions added into LaSrCoO3 under study in the University of Tartu. However, our studies [1-5] indicate that a more effective solution is to increase the reaction volume through the development of MMP structure (G. Nurk, I. Kivi, H. Kurig et al.) (Fig. 1) for the LSCO, PSCO or GSCO cathode and Ni-cermet anodes. In addition to the traditional solid state oxide preparation method, the new solution based synthesis method of LSCO, PSCO and GSCO has been worked out [1-5, 14,15]. The XRD, FIB-SEM, EDX, EDS, XPS, HRTEM, BET, AFM and STM methods have been and will be used for analysis of the materials prepared using different fixed decomposition temperatures, pore forming agent (PFA) and binder amounts, and with different specific surface area (SSA), pore size distribution (PSD), ratio of micro and mesopores areas (S_m/S_m) and volumes (V_m/V_m). Based on the FIB-SEM 3D analysis (R. Kanarbik, P. Møller et al.) (Fig. 2), total porosity of 62±2% and specific surface area of 0.6±0.05 m² g⁻¹ has been calculated. These data are in a good correlation with BET data.

In cooperation with Paul Scherrer Institute (G. Nurk, R. Struis, A. Braun et al.) [11, 19] the formation of multivariable sulphur containing intermediates (SO2, SO3, H2S, SO4²-, SO3²-, S²- etc.) at Ni-Ce0.9Gd0.1O2-δ anode has been demonstrated depending strongly on the electrode potential and on the sulfur containing compound concentration in CH4. Quick electrochemical degradation of Ni-cermet anode has been demonstrated using synchrotron radiation based X-ray adsorption (XANES/EXAFS) spectroscopy and cyclic voltammetry methods.

Ni-free anodes for MT SOFC have been studied in cooperation with the University of Pennsylvania (K. Tamm, R. Küngas, Prof. R.J. Gorte) [13]. For activation of anodes, the impregnation (infiltration) methods have been used and a noticeable increase of activity for Ni-free anodes has been demonstrated. However the degradation of Ni-free anodes was also comparatively quick.
Since 2010, the carbide derived carbon (CDC) based PEMFCs (J. Nerut, E. Härk, K. Vaarmets, S. Sepp, et al.) [16-18] are under intensive study in the chair of PC. It has been demonstrated that the ratio of micro/mesoporous volumes in the carbon support has strong impact on the current and power density values for the catalysts synthesized. The Pt-nanoclusters activated CDC catalysts demonstrate noticeably higher electrocatalytic activity (more than one order of magnitude) compared with traditional microporous carbon (Vulcan XC72R) based catalysts (Fig. 3). In addition, it was established that differently from Pt Vulcan XC72R catalysts based system, our catalysts have very high capacitance values, applicable for electricity storage in PEMFC electrodes. The stored electrical energy can be used for combined electrical cars for the acceleration purposes, thus differently from traditional hybrid systems less volume is needed because the capacitors (capacitive behavior) are already introduced into carbide derived carbon based fuel cells [16-18].

**Fig. 3.** Electrocatalytic activity for Pt-nanoclusters activated CDC based catalysts and for traditional microporous carbon Vulcan XC72R. Various catalysts are noted in the figure.

**Deposition and study of thin film electrodes**

During the last few years the magnetron sputtering method for preparation of thin film has been introduced [20-22] and new single and multilayered thin film materials (Bi, Si, Sb, Pt, Au, C) have been deposited and studied (T. Romann, J. Eskusson et al.) [23,24]. It was demonstrated that thin-film Bi electrodes have anomalous behavior and the s-polarized infra-red (IR) signal component is active, characterizing the surface properties of thin film Bi, Sb and Si electrode layers [25]. In addition it was demonstrated that very clean ionic liquids (RTIL) (cleaned inside the high vacuum chamber under pressure 10^{-8} atm during 48h) demonstrated extremely wide region of ideal polarisability (more than 4.5V) at CDC carbon and different thin layered electrodes. In cooperation with the Institute of Physics (prof. E. Nõmmiste, J. Kruusma et al.) the synchrotron radiation based photoelectron spectroscopy studies have been started, demonstrating that after additional drying of EMIMBF_4 and CDC electrodes inside the high vacuum measurement chamber, nearly 3.5V ideal polarisability region for micro-meso-porous CDC\(\mid\)EMIMBF_4 interface can be achieved. Thus, in principle, the energy and power density of EDLCs can be increased nearly by one order if the extreme conditions for completing of supercapacitors can be used.

**Electrical double layer structure and adsorption kinetics of compounds**

Influence of ionic liquids anion and cation chemical composition and cation hydrocarbon chain structure on the electrical double layer structure has been analysed using experimental and quantum chemical calculation methods (K. Lust, L. Siinor, V. Ivaništšev, C. Siimenson et al.) [26-30]. It was demonstrated that a multilayer electrical interface structure is being formed. However, the first layer has the decisive influence determining the capacitive properties (~85-88%) of the total Bi(111) electrode \(\mid\)RTIL interface. In Situ STM studies data obtained for EMIMBF_4, BMIMBF_4 and EMPyrBF_4 RTILs in contact with Bi(111) electrode surface (E. Anderson, V. Grozovski, P. Pikma)
are in a good agreement with multilayered interfacial conception (Fig. 4). Noticeable influence of the isomeric structure of an organic compound (for example 2,2’ and 4,4’-bipyridine) on the interfacial layer structure (H. Kasuk, G. Nurk et al.) and adsorption kinetics of organic compounds and anions at Bi(111) or Cd(0001) electrode have been demonstrated [33-39].

![Fig 4](image)

**Fig 4.** The in situ STM images of cleaved Bi(111) electrode in EMIM+ BF4- ionic liquid at room temperature under cathodic polarization, at different potentials (a) and (b) respectively.

It has been established that the adsorption layer formation process in uracil, 2,2’-bipyridine, 4,4’-bipyridine, I- and Br- anions containing solutions can be divided into kinetically high rate and low rate processes (M. Väärtnõu, H. Kasuk, L. Siinor, K. Lust, G. Nurk) [33-39]. The rate of short characteristic time adsorption processes depends strongly on the electrode potential (on structure of adsorption layer), surface concentration (i.e. Gibbs adsorption) and chemical properties of solvent.

![Fig 5](image)

**Fig 5.** The in situ STM images of (a) electrochemically polished Bi(111) and (b) cleaved Bi(111) electrode in 3*10-4 M H2SO4 + 0.5 M Na2SO4 aqueous solution under cathodic polarization with (a) adsorbed 2D layer of 2,2-bipyridine and (b) adsorbed 2D layer of 4,4-bipyridine.

Electroreduction of complex anions (Fe(CN)6^3-, S2O8^2-) and cations (Co(NH3)5^3+) (R. Jäger, E. Härk, J. Nerut, S. Sepp) [40-42] has been studied at rotating Bi(111) and Cd(0001) disk electrodes (RDE). Noticeable deviations from the traditional so-called outer-sphere reaction mechanism have been demonstrated based on non-linear least square analysis of impedance spectra. Thus, adsorption of intermediates has been demonstrated and verified by data obtained using RDE, IR and impedance spectroscopy methods.

Since 2010, noticeable attention has been paid on the participation in the international giant project European Spallation Source and development of research capacity in the field of neutron based in operando and in situ studies of the electrochemical power sources and electrode materials. In total 42
Thomson Reuters Web of Knowledge publications have been published and 3 patents (EU, Estonian, Russian Federation) and 1 patent application (USA) have been accepted.

**Current projects of Chair of Physical Chemistry**

- European Spallation Source: Estonian Partition in ESS Instrument design, development and building and application for scientific research (ESSource, PI: E. Lust)
- Estonian Centres of Excellence project: High-technology materials for sustainable development (PI: E. Lust) (Project TK117)
- Estonian Energy Technology Program Project: Development of materials and single cells for solid oxide and polymer electrolyte fuel cells, high temperature electrolyzers and supercapacitors (PI: E. Lust) (Project SLOKT10209T)
- Estonian Material Technology Program Project: Synthesis, characterizing and application of activated rear-earth compounds in fuel synthesis reactors and other high-tech devices (PI: E. Lust)
- Estonian Target Financing Project: Processes at modified phase boundaries and development of novel electrochemical power sources and supercapacitors (PI: E. Lust) (SF180002s08)
- ETF-USA Civil Foundation Project: Development of novel ceramic anode materials for solid oxide fuel cells (PI: E. Lust) (Project SLOKT09123E)
- N-INNER Nordic Energy Research Project: Efficient production of fuels from biomass (PI: E. Lust) (Project SLOKT09123E)
- Estonian Science Roadmap Project: NAMUR-nano particles investigation and application (PI: M. Kirm, E. Lust)
- TU mediumscale infrastructure modernization project: Nanomaterials in sustainable energetics (PI: E. Lust) (TAP-2-15)

**ETF grants:**

- Development of nanoporous electrodes for solid oxide fuel cells (PI: E. Lust) (Project ETF7791)
- Novel ceramic proton conductive membranes for solid oxide electrolysis cell (PI: G. Nurk) (Project ETF8865)
- Development of 3D structural anodes and cathodes for solid oxide electrolysis and fuel cells (PI: P. Möller) (Project ETF8860)
- Development of bilayered cathode on ceria based electrolyte for intermediate temperature solid oxide fuel cell (PI: I. Kivi) (Project ETF9352)
- Interfacial faradic charge transfer and adsorption processes at the room temperature ionic liquid electrode interface (PI: H. Kasuk) (Project ETF8786)
- Microporous carbon supported non-noble metal catalysts for polymer electrolyte membrane fuel cells (PI: J. Nerut) (Project ETF8267)
- Properties of metal and carbon electrodes in ionic liquids (PI: K. Lust) (Project ETF8357)

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