Main Research Developments in the Chair of Colloid and Environmental Chemistry (2007-2012)
Kaido Tammeveski

The research activity of the Chair of Colloid and Environmental Chemistry concentrates on the studies of processes in heterogeneous and nanostructured systems and the development of new analytical tools and methods which can be used for the environmental-friendly treatment of wastes. We are working out mathematical models for transition processes of pollutants in solid and liquid industrial waste with the aim to describe chemical processes occurring with these compounds in environment.

Kinetic studies of oxygen reduction on supported metal nanoparticle-based catalysts
Main research attention of our group is focused on the development of novel electrocatalysts for the oxygen reduction reaction (ORR) since the production of currently used Pt-based catalysts is not economically viable. In order to reduce the cost of proton-exchange membrane fuel cells (PEMFCs), it is ideal to substitute the Pt-based cathodes with cheaper alternatives. Special attention of our studies was devoted to the new synthetic methods for the preparation of supported mono- and bimetallic nanoparticles (NPs) of well-defined size and geometry and investigation of their performance in ORR [1-7]. Carbon nanotubes (CNTs) were utilized as a support material for nanoparticulate metal catalysts. Various strategies have been developed to fabricate gold, palladium and platinum nanoparticles (AuNP, PdNP and PtNP) and the ORR activity of CNT–supported NPs was investigated (N. Aleksejeva, K. Jukk et al.) [1-3]. Several approaches have been employed to prepare Pd-M bimetallic alloys (M = Fe, Co) supported on Vulcan XC-72R carbon [4]. This research was made in collaboration with Prof. J.M. Feliu (University of Alicante, Spain). The influence of different synthetic conditions on the values of specific activity and other kinetic parameters was investigated. Pd nanoparticles and Pd-M nanoalloys exhibited significantly high electrocatalytic activity for the four-electron reduction of O₂ to water. These Pd-based catalysts showed higher ORR activity than bulk Pd. Commercial 20 wt.% and 30 wt.% Au/C catalysts were also used in the oxygen reduction studies (H. Erikson et al.) [5]. A molecular template approach was used for the electrodeposition of AuNPs on the aminophenyl-modified glassy carbon (GC) electrodes [6]. Nanoparticulate gold appeared to be a good catalyst for ORR in alkaline media, whereas the O₂ reduction activity in acid solution was significantly lower. We also employed layer-by-layer (LBL) method to prepare AuNP/MWCNT composites for O₂ reduction (N. Aleksejeva and K. Tammeveski) [7]. Citrate-stabilized AuNPs and poly(diallyldimethylammonium chloride) wrapped MWCNTs were used in the preparation of the composite material. Physical methods can be employed for the deposition of metal nanoparticles on the surface of CNTs. Magnetron sputtering appears to be an efficient technique for the preparation metal nanoparticle/MWCNT composites [8-10]. AuNP/MWCNT catalysts prepared by sputter-deposition possessed good electrocatalytic properties for ORR in acid media (N. Aleksejeva et al.) [8]. AgNP/MWCNT and PdNP/MWCNT composites showed high ORR activity in alkaline solution (L. Tammeveski, K. Jukk et al.) [9,10]. However, the overall O₂ reduction activity of these nanocomposites was still lower than that of Pt/C catalysts in 0.1 M KOH.

Electrocatalysis of oxygen reduction on thin metal films and shape-controlled PdNPs
Vacuum deposited thin films of an active metal on a less active substrate consist of small islands and can therefore be regarded as the simplest type of nanostructured catalyst on which the effect of the metal particle size and possible metal-support interactions can be studied. The most active metal catalyst for ORR is platinum, but considerable attention has been also paid to Pd, due to its lower cost. O₂ reduction on thin Pt and Pd films (nominal thickness 0.5-20
nm) deposited onto glassy carbon or Au supports has been studied in different solutions: H$_2$SO$_4$, HClO$_4$ and KOH (A. Sarapuu, H. Erikson et al.) [11-14]. This research was made in collaboration with Prof. K. Kontturi (Aalto University, Finland). It was demonstrated that the mechanism of O$_2$ reduction on thin-film electrodes is similar to that on bulk Pt and Pd. The specific activity of metal catalysts did not remarkably depend on the support material [11-14]. On thin Au films on GC, two-electron reduction of O$_2$ to hydrogen peroxide prevailed in acid solution, but in alkaline media, the activity was higher and 4e$^-$ reduction was observed at low overpotentials [15]. Recently, we electrodeposited Pd coatings onto GC and Au supports and found that these catalysts possess high ORR activity in alkaline media (H. Erikson et al.) [16]. The shape-controlled synthesis of metal nanoparticles enables to design more active catalysts for O$_2$ reduction. Pd nanocubes were synthesized by Dr. J. Solla-Gullón (University of Alicante, Spain) and their average size was 27 nm. Cubic PdNPs showed considerably higher ORR activity in alkaline and acid solutions as compared to spherical PdNPs or bulk Pd (H. Erikson et al.) [17,18]. This increased activity is probably due to the predominance of Pd(100) surface sites that show weaker adsorption of (bi)sulfate anions than Pd(111) facets. The 4-electron reduction of O$_2$ was observed on the Pd catalysts studied and the Tafel analysis revealed that the mechanism of the ORR on PdNPs is the same as on bulk Pd or Pt [17,18].

**Oxygen reduction on carbon nanomaterial based catalysts for low temperature fuel cells**

In the cost point of view there is a huge interest in developing fuel cell electrodes with lower amount of noble metal or non-noble metal catalysts for ORR. The electrocatalytic activity of carbon nanomaterials toward O$_2$ reduction is of great importance, because of the possibility of using them as support material for various catalysts in fuel cell applications. Recently we have studied different carbon nanomaterials as possible electrocatalyst supports for ORR (I. Kruusenberg, N. Aleksejeva et al.) [19-25]. In collaboration with Skeleton Technologies (Tartu, Estonia), the ORR activity of carbide-derived carbons (CDC) was investigated in alkaline media [19]. We have studied the reduction of O$_2$ on double-walled carbon nanotube (DWCNT) modified electrodes in acid and alkaline solutions [20]. The pH dependence of O$_2$ reduction on MWCNT-surfactant modified GC electrodes has been also investigated [21]. It was found that CNTs are active catalysts for ORR at high pH. We demonstrated that carbon support material properties influence the kinetics of the ORR drastically [22]. In addition we studied the effect of acid treatment of single-walled and multi-walled carbon nanotubes on the ORR activity [23]. The O$_2$ reduction results showed that Fe impurities are responsible for the electrocatalytic activity of CNTs. The electrocatalytic properties of acid-washed MWCNTs were studied also in alkaline media using hydrodynamic electrode modification method [24]. It has been found that nitrogen-doped carbon materials (such as graphene, carbon nanotubes, ordered mesoporous carbon, etc) could act as effective metal-free catalysts. It has been established that the doped nitrogen atoms such as graphitic-N, pyridine-N, and pyrrole-N play a crucial role in the ORR. N-doped carbons could serve as alternative cathode materials to Pt-based catalysts for fuel cells. This has been demonstrated using vertically aligned N-doped carbon nanotube modified electrodes in acid and alkaline media (N. Aleksejeva et al.) [25]. We have also used post-treatment procedure for N-doping of MWCNTs and graphene sheets. Heat-treatment in the presence of urea was used for that purpose (M. Vikkisk et al.) [26]. In collaboration with Dr. A.M. Kannan (Arizona State University, USA) we studied the reduction of O$_2$ on iron phthalocyanines (FePc) and cobalt phthalocyanines (CoPc) supported MWCNT catalysts (I. Kruusenberg et al.) [27]. These FePc/MWCNT and CoPc/MWCNT catalysts were tested as alternative cathode materials to Pt/C in alkaline membrane fuel cell (AMFC) using Tokuyama A201 membranes. NM$_4$-macrocycle catalysts possessed excellent electrocatalytic properties comparable to that of commercial Pt-based catalysts (see Figure 1).
Heat-treatment of MN₄ macrocycle/MWCNT is crucial to increase their durability and ORR activity. The highest activity was observed by pyrolyzing these materials at 800 °C [28].

![Figure 1](image.png)

**Figure 1.** Fuel cell performance of MEAs with Co and Fe phthalocyanine modified MWCNTs along with pure MWCNTs and Tanaka Pt/C catalysts based cathodes using Tokuyama’s A201 series anion exchange membrane.

**Electrochemical properties of aryl-modified electrodes**

Chemically modified electrodes can be used for various applications, including electrocatalysis and electroanalysis. We have systematically studied the electrochemical behavior of aryl-modified glassy carbon (GC), nickel and gold electrodes [29-45]. This research has been made in collaboration with Prof. D.J. Schiffrin (University of Liverpool, UK). The electrodes were modified by the electrochemical reduction of aryl diazonium salts. This is a convenient and versatile method of surface modification. GC electrodes were electrografted with various aryl groups (phenyl, naphthyl, anthracenyl, biphenyl, 4-bromophenyl, 4-decylphenyl, 4-nitrophenyl, 4-carboxyphenyl, azobenzene, etc). Ferricyanide reduction was blocked to a much larger degree than O₂ reduction (M. Kullapere, E. Kibena et al.) [29-31]. The electron transfer process of 2,2’-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) on aryl-modified GC was also investigated (E. Kibena et al.) [32]. Thick films of anthraquinone (AQ) grafted to GC surface showed an interesting electrochemical behavior toward the Fe(CN)₆³⁻ [33,34] and Ru(NH₃)₆³⁺ redox probes [33]. GC electrodes were modified with 9,10-anthraquinone and 9,10-phenanthrenequinone and O₂ reduction was studied on these electrodes as a function of pH (G. Jürmann et al.) [35]. The spontaneous grafting of GC with AQ was achieved by immersion of the substrate in the solutions of AQ diazonium salt for different periods of time (J.-M. Seinberg et al.) [36]. The electrocatalytic activity of spontaneously grafted AQ for O₂ reduction was similar to that of the electrochemically grafted electrodes. The GC surface modification with *in situ* generated AQ diazonium cations is similar to that observed for pre-synthesized AQ diazonium salts. GC electrodes modified in acetonitrile and in aqueous acidic solution showed similar electrocatalytic activity for O₂ reduction (M. Kullapere, et al.) [37]. Surface modification using AQ carboxylates was also achieved [38]. The O₂ reduction activity of various quinones deposited on HOPG depended on the redox potential of the quinones (A. Sarapuu et al.) [39]. Anthraquinone derivatives covalently attached to high-area carbon materials can be used as a cathode for the electrochemical production of hydrogen peroxide in fuel cell conditions [40]. The reduction of oxygen was also studied on AQ-modified Ni electrodes and a high electrocatalytic activity for this reaction was observed (M. Kullapere and K. Tammeveski) [41]. The blocking effect of nitrophenyl films electrografted to Ni electrodes on the electron transfer processes of the Fe(CN)₆³⁻/⁴⁻ redox couple was in evidence (M. Kullapere et al.) [42]. Electrografting of Au electrodes with aryl diazonium salts in acetonitrile yielded strongly attached films (M. Kullapere et al.) [43-45]. The modified Au electrodes were characterized using AFM, EQCM and XPS techniques. Cyclic voltammetry revealed a quasi-reversible
response of surface-confined AQ in 0.1 M KOH [43]. AFM studies revealed granular growth of aryl films. This finding is also supported by the XPS data where the Au 4f peaks are clearly seen for the electrodes of high surface concentration of 4-bromophenyl and 4-nitrophenyl groups [44]. The electrochemical response of the Fe(CN)$_6^{3-}$ probe was completely suppressed on 4-nitrophenyl modified Au electrodes and less suppressed on 4-decylphenyl modified Au electrodes. The kinetics of O$_2$ reduction was inhibited to a lesser extent on both modified electrodes as compared to that of the Fe(CN)$_6^{3-}$ probe (M. Kullapere et al.) [45].

**Main Research Developments in the Laboratory of Biosensors.**

Modern society and the rapidly increasing number of people along with the higher standards for the quality of life have raised the demand for real-time monitoring and control of the potentially harmful compounds in environment and food. Although the application of traditional chemical or microbiological methods provide excellent results, concerning the sensitivity and selectivity of analyses, these methods are time-consuming and do not enable automatic feedback to minimize negative effects on health and environment. So biosensors, defined as analytical devices combining molecularly recognizing materials with a signal transducer and generating a measurable signal as a result of interaction with a specific analyte, present a good option to solve the problems of real-time analyses.

We have studied the construction and signal rising of different biosensors and biosensor arrays for more than 10 years. For the production of biosensors with exchangeable enzyme-containing threads, enabling an easy and comfortable determination of the amount of different enzymes in the units of lengths, a novel technological solution has been proposed [46,47] and a patent granted. A lot of attention has been paid to the problems of biosensor signal modeling and determination of optimal parameters for biosensor calibration. As one of the main goals is to obtain results in minimal time, we have focused to the signal rising in transient phase conditions [48]. To enable the calibration and application of biosensor systems showing lower selectivity, we have proposed models for signal analysis and methods for calibration of several substrates in the mixtures of biogenic amines [49-51]. The speeding up of the signal rising in biosensors by modulating the specific bio-recognition reactions has been studied in cascaded lactose biosensors [52,53].

An issue not less important in biosensor studies is the quality of the bio-selective recognizing material – its selectivity, activity and stability. We have isolated and purified different oxidases and antibodies and optimized their immobilization onto insoluble carriers [54,55].

For the development and application of biosensor based analytical systems we have carried out several R & D projects in cooperation with industrial partners and research institutions. Our last activities have been focused on the development of biosensors and biosensor arrays for online milk quality and mastitis detection. Although milk is one of the most important products of bestial origin and its quality has a great impact on our health, at present there is no equipment available to determine its quality in real time. We have proposed an on-line system and method of its calibration for simultaneous detection of antibiotic residues in milk, which prototype has been tested in lab conditions and farms (Figure 2).
In addition, we have proposed a sensor based method for a rapid non-invasive detection of mastitis, the most common infection of dairy cattle, in real time. The above-mentioned technologies have both been granted patents in Estonia [56,57]; patent applications in other countries incl. USA, Russia, Australia, China and European countries are pending. Based on the needs of milk producers, the mastitis sensor is planned to be complemented with an immunosensor, enabling a quick identification of selected mastitis – causing pathogens.

Retorting process of oil shale and its environmental impact
Oil shale semicoke is a solid waste resulting from oil shale retorting and is classified as hazardous waste in the Estonian Waste List. The data presented confirmed that the leaching of heavy metals is not a problem in case of oil shale semicoke, but the leaching of organic compounds may exceed the limit for TOC due to an operational mistake during the retort process (K. Orupõld et al.) [58].

Due to the elevated concentrations of heavy metals Cd (25 mg kg⁻¹), Zn (3630 mg kg⁻¹), Ba (4260 mg kg⁻¹), and Hg (1.7 mg kg⁻¹) landfill deposition is the only reasonable alternative for cyclone ash, because a major part of the heavy metals retained in cyclone ash are not easily liberated under the conditions normally found in nature (R. Pöykiö et al.) [59]. The choice of adsorbent for leachate treatment is important to remove the heavy metals and the results of leaching tests showed that adsorbents based on peat are suitable for heavy metal (Cd, Pb, Ni) ions, having 3–10 times higher capacity than semi-coke and pine bark (Ü. Sõukand et al.) [60], but surfactants can influence the leaching process (A. Selberg et al.) [61].

Polyvinylidene fluoride particles and film were chemically modified by grafting with polystyrene without a preliminary treatment of the fluoropolymer surface. The amount of covalently bound polystyrene was quantified using Fourier transform infrared spectroscopy and the extent of grafting was found. The formation of polystyrene brushes was observed via scanning electron microscopy (J. Liiv et al.) [62].

The impact of oil shale mining on water ecosystem depends on the location of the mine, the mining technology, the hydrology and climate of the area and the physical-chemical properties of the oil shale and by-products. The mine water pumped out is directed through outlet ditches and rivers mainly into the Gulf of Finland, but also into Lake Peipus. During ten years (1995-2005) the concentration of total nitrogen in the samples of the river water from the Pühajõgi catchment has decreased on the average almost 90%, while the conductivity values of the river water samples of the Pühajõgi catchment between 800 and 1800 µS cm⁻¹ indicated a significant amount of ionic species in the river water (A. Selberg et al.) [63,64]. Beside of pollutants the quality of surface water is influenced by natural organic matter (NOM) which is a complex of substances. Analysis of water from the bog lake showed relatively high content of macromolecular organic compounds rich in aromatics, whereas water samples from the mire feeding river contained predominantly more homogeneous low-molecular-weight materials poor in aromatics (A. Selberg et al.) [65].

Phenolic compounds are listed as priority environmental pollutants and the wastewater from the oil-shale chemical industry in North-eastern Estonia is treated at the Kohtla-Järve wastewater treatment plant (WWTP). The obtained results indicated that the microbial community of activated sludge was able without an adaptation to oxidize phenol, 5-methyioresorcinol and resorcinol, but the activated sludge degraded resorcinol and 5-methyioresorcinol more slowly than phenol (R. Lepik and T. Tenno) [66]. The obtained interaction parameters for the studied bi-substrate systems indicated that phenol had a stronger inhibition effect on the biodegradation of p-cresol than p-cresol had on the biodegradation of phenol, while o-cresol had a stronger inhibition effect on the biodegradation
of phenol, which in turn had a mild inhibition or even enhancing effect on the biodegradation of o-cresol (R. Lepik and T. Tenno) [67]. Interaction of retorted shale with water generates highly alkaline leachate with a high content of sulfur due to different chemical reactions. Part of the sulfur is emitted into the atmosphere due to a gaseous hydrogen sulfide generating atmospheric pollution. The system of solid CaS in equilibrium with water will contain, on a significant level, six different species in the water phase: Ca$^{2+}$, S$^{2-}$, HS$^{-}$, H$_2$S, OH$^{-}$ and H$_3$O$^+$. For calculations of essential parameters of the equilibrium state, a simplified system of equations, describing the behavior of solid calcium sulfide in contact with water has been developed (I. Zekker et al.) [68]. The average time required to achieve the equilibrium of H$_2$S in the wastewater was 16.2 min (A. Selberg et al.) [69]. The measurements resulted in the solubility of CaS as 1.73 mmol/L (I. Zekker et al.) [68]. The behavior of strontium sulfide (SrS) in water is quite similar to CaS, but solubility of SrS was evaluated to be 1.67 mM/L (K. Uiga et al.) [70].

**Determination of biodegradable organic substance and their biodegradability**

Aeration is the most energy-consuming process in biological wastewater treatment, whereas impaired oxygen permeability caused by various chemicals at the air–water surface plays an important role in industrial wastewater treatment facilities. The results of study showed that the influence of the surfactant on the oxygen permeability at very low concentrations was much more significant than the effect on surface tension (E. Mölder et al.) [71]. Determination of biodegradable organic substances in wastewater has significant importance on the environmental pollution control and it is characterized mainly through biochemical oxygen demand (BOD) which can be determined by biosensors with mixed microorganisms and activated sludge immobilized within a single membrane onto an oxygen sensor. Their calibration results showed that steady-state and dynamic method of measurements are both reliable tools for BOD estimations (S. Velling and T. Tenno) [72]. The results of the BOD values determined by BOD biosensor for wastewater samples with OECD degradation index in the range 0.43–0.61 is approximately 13% higher than experimental BOD$_7$. Analyses of refractory wastewater (BOD$_7$/COD ratio 0.3 in average) showed an underestimation in BOD$_7$ of 4–10% (S. Velling et al.) [73]. BOD values for dairy industry wastewater obtained with current semi-specific biosensors considerably overestimate BOD$_7$, while universal biosensors underestimate BOD$_7$ obtained by the conventional 7-day BOD test (M. Raud et al.) [74].

**Autotrophic nitrogen removal by anaerobic ammonium oxidation method**

Nitrogenous wastewaters with a low C to N ratio (COD/TN ratio ≤ 3) are generated in several domestic and industrial waste management processes. Novel short-cut biological nitrogen removal methods, such as combined partial nitritation-anaerobic ammonium oxidation (anammox), save about 60% of the aeration, 90% of the sludge handling and transport, and 100% of the organic carbon addition (E. Rikmann, I. Zekker et al.) [75,76]. Some aspects like the accelerating effect of intermediates (mainly N$_2$H$_4$ and NH$_2$OH) of anammox bacteria have been studied specifically in lab-scale to clarify the metabolism of these unique energetically conservative microorganisms. Experiments in a moving bed biofilm reactor and batch tests (I. Zekker et al.) [77] were performed to evaluate the optimum concentrations of anammox process intermediates that accelerate the autotrophic nitrogen removal (I. Zekker et al.) [78].

**Projects of the Chair of Colloid and Environmental Chemistry (2007-2012)**

- Removal of persistent pollutants from the wastewater by physial-hemial and biological methods to decrease the pollution of environment (CHEMBIO) (PI: T. Tenno and M. Trapido (TTU) (Project AR12017)
• Optimization of biochemical methods for the biogas generation in anaerobic digestion and development their monitoring and control (PI: T. Tenno) (Project 3.2.0501.10-0020)
• Applied study of autotrophic nitrogen removal technology (PI: T. Tenno) (Project SLOKT11119)
• Reduce of CO₂ emission through increased oxygen content in fluidized bed incinerator (PI: T. Tenno) (Project SLOKT12034T)
• FIBONACCI – Large scale dissemination of inquiry based science and mathematical education (PI: T. Tenno) (Project MLOKT09172R)
• Processes in macro-and microheterogeneous and nanoscale systems and related technological applications (PI: T. Tenno) (Project SF0180135s08)
• Seed cities for science: a community approach for a sustainable growth of science education in Europe (PI: T. Tenno) (Project MFKFE06040R)
• Preparation of pilot samples of materials (PVDF, PEI, PETE) for measurement of electretic properties (PI: T. Tenno) (Project LFKFE07092)
• Management of waste water with high nitrogen content (PI: T. Tenno) (Project SLOTI08262)
• Processes at interfaces and in condensed phases and their application in environmental technologies (PI: T. Tenno) (Project SF0182537As03)
• Renovation of science teaching in European primary education with inquiry methods (PI: T. Tenno) (Project MFKFE05093R)
• Application of anaerobic nitrogen removal processes for treatment of diverse wastewater systems (PI: T. Tenno) (ARCI-MEDES, 02.09 2012 -01.06.2015)
• Optical biosensor system for the detection of antibiotics in milk (PI: T. Rinken) (Project ILOKT08010)
• Production and testing of laboratory prototype of the optical biosensor system for the detection of milk quality (PI: T. Rinken)
• ETF-U.S. Civilian Research & Development Foundation (CRDF) grant: Investigation of the kinetics of oxygen reduction on nanostructured new cathode catalysts for low-temperature fuel cells (PI: K. Tammeveski) (Project SLOKT10101E)

Estonian Research Council (former Estonian Science Foundation) grants:
• Electrocatalytic oxygen reduction on carbon nanotube-based electrodes (PI: K. Tammeveski) (Project ETF9323)
• Electrochemical reduction of oxygen on non-platinum catalysts (PI: A. Sarapuu) (Project ETF8380)
• Electrochemical reduction of oxygen on nanostructured and nanocomposite materials (PI: K. Tammeveski) (Project ETF7546)
• The study of individual and cooperative effects of antibiotics on enzymatic activity with biosensor systems (PI: T. Rinken) (Project ETF7465)
• Multivariate modeling of biosensor systems towards different compounds in mixtures (PI: T. Rinken) (Project ETF9061)
• Alternative ways of anaerobic ammonium oxidation process and the ways of its usage. (PI: A. Menert, T. Tenno) (Project ETF9370)
• Investigation of oxygen mass-transfer through the air-water interface (PI: T. Tenno) (Project ETF7170)

References:


66. R. Lepik, T. Tenno, Biodegradability of phenol, resorcinol and 5-methylresorcinol as single and mixed substrates by activated sludge. Oil Shale 28 (2011) 425–446.


70. K. Uiga, T. Tenno, I. Zekker, T. Tenno, Dissolution modeling and potentiometric measurements of the SrS–H2O–gas system at normal pressure and temperature at salt concentrations of 0.125–2.924 mM. Journal of Sulfur Chemistry 32 (2011) 137-149.


