The key aim of research activities covered by this doctoral dissertation was to develop cost effective and durable under long-term operation, advanced Ni foam-based electrocatalyst materials, as highly effective cathode and anode electrodes for hydrogen evolution (HER) and oxygen evolution (OER) reactions, respectively. In addition to their long-term durability, highly efficient electrode materials should primarily be characterized by low overpotential values for the corresponding electrochemical processes. It is commonly known that the process of water splitting is driven above the thermodynamic requirement of 1.229 V. Moreover, the catalyst substrates should not only be based on materials that are abundant in natural environment, but they should also be characterized by high electrical conductivity and extended, electrochemically active surface area.

Thus, in the first part of this work, a comprehensive study on the kinetics of the HER cathodic process is presented. The HER was examined at innovative, composite catalyst materials, such as: *as received* nickel foam (Ni foam) and Ni foam base material modified with very small amounts of iridium nanoparticles. Two methods of metal deposition were implemented here, i.e. spontaneous and electrochemical surface deposition. All electrochemical examinations were performed in a three-compartment, pyrex glass-made electrochemical cell in 0.1 M NaOH electrolyte solution, prepared by means of a Direct-Q3 UV ultra-pure water purification system from Millipore (18.2 MΩ cm water resistivity), at room temperature. Electrochemical impedance spectroscopy and *quasi* steady-state polarization methods were employed through the operation of the *Solatron 12,608* W Full Electrochemical System, consisting of 1260 Frequency Response Analyzer (FRA) and 1287 Electrochemical Interface (EI). In addition, spectroscopic characterization of catalyst materials was performed by means of SEM/EDX (Scanning Electron Microscopy/Energy-Dispersive X-Ray Spectroscopy) analyses.

Based on the recorded charge-transfer resistance, exchange current-density, interfacial capacitance and other parameters, it was reported that very low amounts of Ir deposit on the surface of pre-treated Ni foam materials caused a radical enhancement of their HER catalytic activity. The obtained results clearly indicated significant opportunities for the Ir nanoparticle-modified Ni foam composites towards the HER process and their possible employment in commercial, alkaline water electrolysers.

The effectiveness of complex water splitting process depends on the kinetics of both the HER and OER electrode reactions. While the cathodic hydrogen evolution is characterized by relatively low overpotential values, the OER remains a major factor that controls the overall rate of water decomposition process. Therefore, the second part of this thesis is concerned with the OER reaction's kinetics. The latter was also examined on the catalytically modified Ni foam materials. Hence, small amounts of platinum, freshly prepared transition metal-based electrocatalysts (cobalt and molybdenum) and extensively electrooxidized Ni foam electrodes were selected as anodes. Interestingly, the OER catalysts prepared based on non-noble metals proved to be beneficial, when compared to both the Pt-modified and electrooxidized Ni foam electrodes, which exhibited inferior OER electrochemical activity.

In the last part of this work, practical examinations of alkaline water electrolysis were carried-out by means of an innovative, 500 W laboratory size AWE (Alkaline Water Electrolyser) system, equipped with Pd-activated Ni foam or unmodified Ni foam cathodes, and *in situ* electrooxidized Ni foam anodes. The total catalytic activity and stability tests (dc. galvanostatic and ac. impedance measurements) of the proposed AWE system were carried-out by means of the *Solatron 12,608* W Full Electrochemical System and 30 V/30 A dc. power supply unit (PeakTech®). On the other hand, during the H_2O electrolysis process, samples of O_2 and H_2 gases were collected and analyzed with the use of a gas chromatograph (GC) Shimadzu GC2014 model, equipped with a chromatographic column and a helium detector with

pulse discharge (PD-HID-Pulsed Discharge Helium Ionization Detector). It was reported that the AWE system equipped with the unmodified Ni foam cathodes (in combination with surface-electrooxidized Ni foam anodes) achieved a maximum power of about 500 W, whereas that of the Pd-modified Ni foam cathodes reached 560 W. Moreover, both generated H_2 and O_2 gas products were high purity (H_2: 99.99% and O_2: 99.90%).

Finally, extended-time alkaline water electrolysis experiments were conducted on a single cell electrolyser setup with two different anodes. The cell's configurations comprised Ir-modified Ni foam cathode, whereas anodes were based on either electrooxidized, or else on Co-activated nickel foam electrode. Both electrode arrangements were characterized by similar cell's voltages to those previously reported for the Pd-activated Ni foam cathode/ electrooxidized Ni foam anode. Moreover, these new catalyst systems proved to be fairly durable and stable over the 24-hour galvanostatic tests.