

Capacitive Deionization for selective separation of lithium salt from aqueous solutions

Anna Siekierka

For selective separation of lithium salts from aqueous solutions, the capacitive deionization with its membrane variant and battery desalination were integrated. The new technique was discovered and called hybrid capacitive deionization. The primary cell of HCDCI is consisted of: 1) cathode made of lithium adsorbent (lithium-manganese-titanium adsorbent) and 2) anode made of activated carbon covered with anion exchange membrane. This system has been used to separate lithium salt from monocomponent solution (LiCl, NaCl, KCl) as well as from real samples. Taking into account construction of the HCDCI system and various lithium ions resources, the following investigations were conducted: 1) preparation and characterization of lithium-manganese-titanium adsorbents; 2) preparation and characterization of anion exchange membranes; 3) the use of monocomponent solutions as feed; 4) testing the HCDCI system for geothermal solutions; and 5) determination of ion adsorption mechanism.

The lithium-manganese-titanium adsorbents were sintered by lithium and manganese carbonates and titanium dioxide. The adsorbents were obtained into three batches: 1) with various partition of titanium dioxide (from 0% to 20%) while the same ratio of lithium and manganese 2) with changing the ratio of lithium and manganese for 5% content of titanium dioxide and 3) preparation adsorbent at 900°C. It has been found sorbent properties showed nonlinear properties with the content of titanium dioxide. The adsorbent with a 5% wt. of titanium dioxide was characterized with the best crystallographic structure, micropore size and good surface wettability.

The next stage of research dealt with preparation of anion exchange membranes. They were obtained by chemical modification of polymer: poly(vinyl chloride) and poly(vinylidene fluoride) by aliphatic amines: ethylenediamine and diethylenetriamine. The obtained anion exchange membranes were characterized by FTIR analysis and by physicochemical methods: ion-exchange capacity, water adsorption and surface surface. Additionally, proton exchange conductivity of each of the obtained membranes was determined by means of impedance spectroscopy. Analysis of the properties showed that the best membranes were EDA-functionalized.

In order to verify the efficiency of the HCDI system, geothermal water was used as a potential source of lithium ions. During the tests, the configuration of the HCDI process was established that enabled 100% of desorption and isolation of lithium salt in a separate stream. Detailed analysis of electrical modes were performed, which directly determine the success of extraction of lithium salt. The most effective electronic mode was found to be CV-ZVC-RCV. By shortening the adsorption time to 180 s and adding the additional desorption operation, it was possible to separate the lithium salt with more than 70% efficiency. In addition, an extremely high total adsorption capacity over 800 mg/g was achieved, that was six times higher than the values reported in literature.

The final evaluation of the sorption mechanism was based on comparison of two theoretical models. The first was modified Donnan model, assuming that the adsorption process takes place in a double layer of sorbent material. The second model was associated with Faradic reactions. Based on obtained adsorption data, it was proved that the dominant mechanism for the HCDI process was related with Faradic reactions.

In the case of geothermal water, the material analysis was carried out by XRD. The obtained data confirmed the change of crystal structure due to insertion of lithium ions into the structure of LMTO. Additionally, by application electrochemical tests, the formation of passive SEI layer on the surface of the selective electrodes was confirmed.