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Model passivated carbon electrodes for fluorine generation in molten KF-2HF electrolyte

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Elemental fluorine is used in the nuclear industry for the isotopic separation of uranium-235 and 238, as well as the purification of LiF-BeF_2 (FLiBe) in molten salt reactors. Elemental fluorine is generated on an industrial scale through electrochemical processes; however, due to the reactivity of fluorine typical electrode components made of metals, such as Cu, Fe, or Ni, are unsuitable in this environment. The electrolyte used for F_2 generation is KF-2HF. Carbon electrodes are used for industrial fluorine generation due to its relatively low cost, high conductivity, and chemical stability. One issue faced using carbon electrodes in this system is electrode passivation through the formation of C-F compounds, which results in a loss of anode wettability in the electrolyte and diminished charge transfer. This leads to high overvoltages for the fluorine evolution reaction (FER), which negatively impacts the safety of the system, increases operation costs, and leads to faster degradation of the electrode.

Carbon electrode passivation in KF-2HF has been relatively well studied. The degradation of electrical characteristics is progressive, ultimately leading to electrode deactivation. It is generally agreed that the process of deactivation begins with a fluoride-passivated surface at potentials above the equilibrium potential (3.85 V). The passivated C-F layer is both insulating and non-wetting to the KF-2HF media. It first inhibits fluorine bubble detachment from the surface of the electrode, leads to the formation of a persistent gas layer and finally, deactivation as the electrode surface is completely covered by this gaseous layer and charge transfer ceases. Only a small current is able to flow even at high potentials (up to 9 V), completely inhibiting fluorine generation. The purpose of this study is to examine the non-wetting properties of a fluorinated surface by using artificially passivated electrodes formed by embedding PTFE-particles in carbon. This should yield a reproducible surface for electrode performance studies that will lead to a better understanding of the surface chemistry. The research will lead to the development of novel electrodes that minimize the overvoltage required for fluorine production. Decreasing the FER overvoltage in industrial applications will enhance the efficiency in the overall process and lower the manufacturing costs for fluorine.

Carbon electrodes with different PTFE-content (between 0 and 35%) were synthesized at elevated temperatures using a press. Electrochemical fluorination was then carried out for different potentials in the fluorine generation region (0 to 9V) in molten KF-2HF electrolyte at ~ 90 °C. The electrochemical behaviour of these carbon-PTFE electrodes were compared to both passivated and non-passivated graphite and amorphous carbon electrodes. The correlation between the amounts of embedded PTFE with the degree of passivation on carbon electrodes will be discussed. This factor was used to compare the non-wetting characteristics of an electrochemically passivated carbon electrode to those of artificially “passivated” electrodes. The PTFE content of the embedded electrodes was measured using TGA. Surface morphology of fluorinated and non-fluorinated carbon electrodes will be presented. The effect of surface and sub-surface C-F compounds on the electrical properties of the different electrodes was correlated to the PTFE content, using AC impedance.