WP5 TASK 5.2

Energy efficient CO_2 electrolysis

ABSTRACT

Carbon capture and utilization (CCU) is a viable approach to convert atmospheric CO_2 into various valuable end products such as fuels, chemicals, and construction materials. In the context of CCU, this research focuses on the conversion of CO_2 to elemental carbon via molten carbonate electrolysis. The effect of electrolyte selection, electrolysis temperature, and cathode material on the specific energy consumption and carbon morphology produced was studied in this work. The focal points of the experimental work were selected based on a lack of previous studies and/or previous studies having contradictory results. Previous studies related to CO_2 conversion in molten salts indicate that the produced elemental carbon can exist in various morphologies, such as carbon nanotubes (CNTs), nanofibers (CNFs), nano-onions (CNOs), platelets, and amorphous carbon.

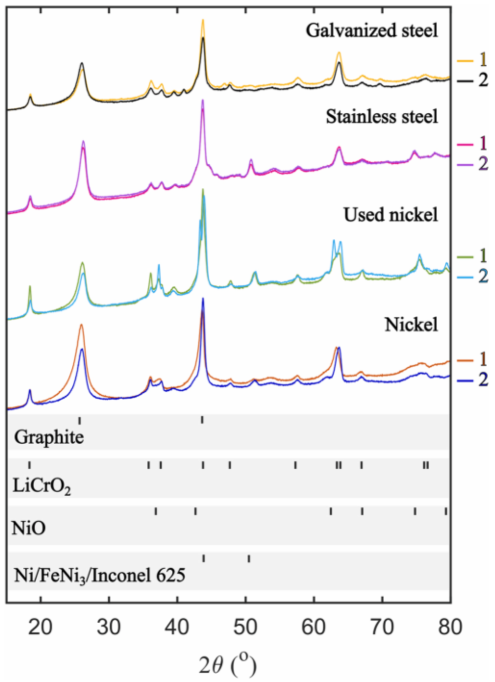
MOTIVATION

To make molten salt electrolysis competitive option for traditional fossil-based carbon production methods process energy consumption needs to be minimized while high quality of carbon product is granted. In a high temperature electrochemical process material selection and controlling electrode degradation is essential. In addition to electrolyte and electrode materials selection, process conditions optimization is a key for a competitive process.

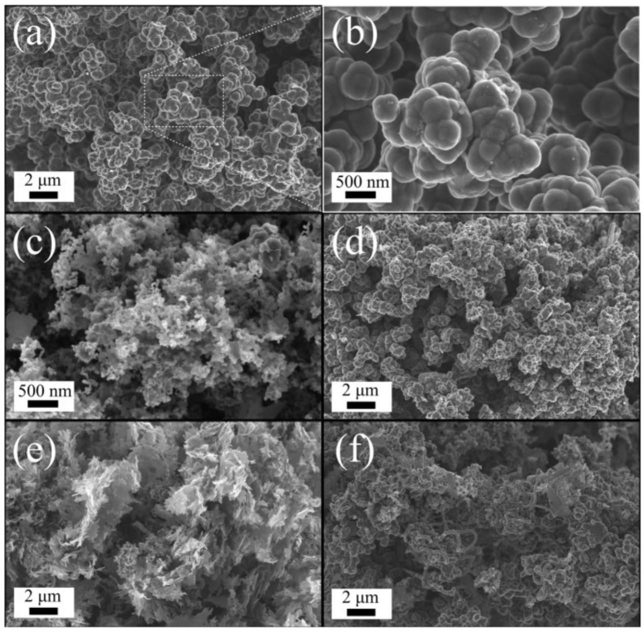
RESULTS

The experimental work was conducted with two different types of electrolyser setups: coaxial and planar. One of the key challenges encountered in the design and selection of materials for these setups is the harsh process conditions. The combination of molten salt, high temperatures, and the generation of oxygen in the process make the process conditions extremely corrosive. Corrosion is producing metallic impurities and those getting mixed with carbon is an issue of concern, as any impurities affect the product quality.

A comprehensive understanding of the produced carbon was achieved through the utilization of various analytical methods, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). The results revealed that the different metals dissolved from the electrodes affect the carbon produced and its morphology. Different metals and different amounts of metals seem to have different types of effects. With little to no dissolved metals mixed with the product, spherical nano-onions were the dominant product. These spherical, onion-like structures were the main product when using nickel cathode. With the presence of iron, tubular structures were dominant, as the iron acted as a nucleation seed for tube growth. Tubular structures were found when steel-based cathodes, both stainless and galvanized steel, were used. Generally, it seems that impurities cause inconsistent products containing various carbon morphologies.



A)

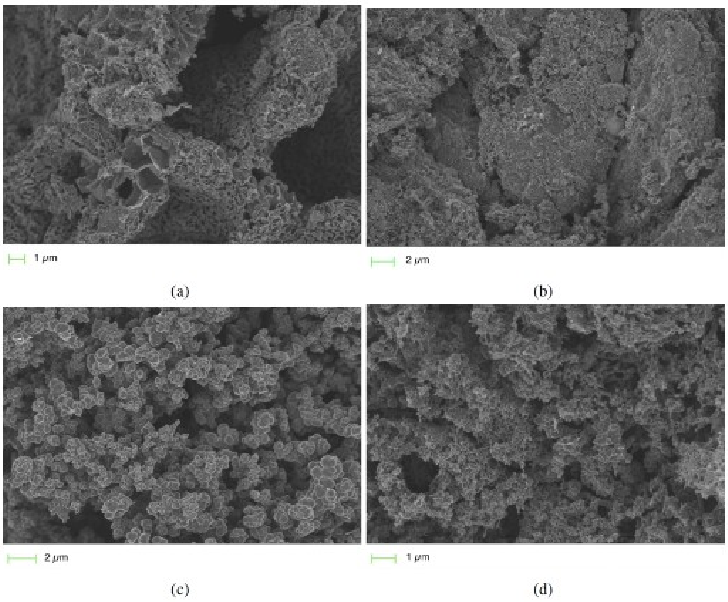


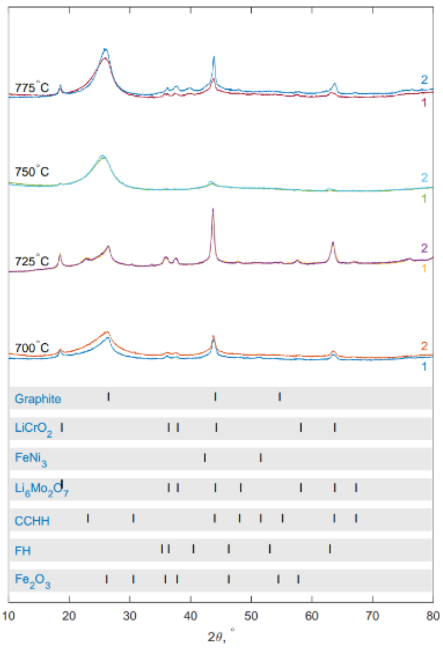
B)

Figure 1. A) XRD patterns of the carbon samples produced with different cathode materials at otherwise fixed conditions. The number of the sample is marked on the right side of the figure, and the most significant peaks for the main identified phases as a function of diffraction angle at the bottom of the figure. B): SEM images of nickel cathode samples: (a) the major morphology of the samples is nano-onions, (b) a higher magnification of nano-onions, (c) significantly smaller spherical structures, (d) more irregular shapes, (e) platy structures, and (f) tubular structures.

In addition to electrode materials, the work studied the effect of electrolyte composition and electrolysis temperature on the carbon morphology produced. Electrolytes studied were Li_2CO_3-$BaCO_3$ and Li_2CO_3-$CaCO_3$ 80:20 mol%. The results showed that both electrolyte composition and electrolysis temperature affect the carbon morphology. The effect of the electrolyte composition was more significant at lower temperatures, as the product morphology differed considerably between the electrolytes. The number of tubular structures increased along increasing temperature in both electrolytes, which indicates that the effect of the electrolyte is not as significant at higher temperatures. Based on XRD diffraction patterns, it can be concluded that not only the morphology of the carbon changes, but also the type and number of metallic impurities.

The results from Li_2CO_3-$CaCO_3$ electrolyte show more promising compared to results from Li_2CO_3-$BaCO_3$ electrolyte in terms of product quality. Regarding electrolysis power and voltage efficiency, Li_2CO_3-$CaCO_3$ proves equal or superior to other electrolytes, depending on temperature. Heat generation occurs in all the experiments, which emphasizes the importance maintaining a constant electrolysis temperature in industrial processes to manage heat generation effectively. Further upscaling process to industrial scale was studied in HYGCEL WP5 task 5.3.





A) *B)*

Figure 2. A) SEM images and B) XRD patterns of carbon produced in Li_2CO_3-$CaCO_3$ electrolyte at a) 700 C, b) 725 C, c) 750 C, and d) 775 C temperature with otherwise fixed conditions.

APPLICATIONS and IMPACT

Molten carbonate electrolysis is still in the development i.e., it has not yet reached a commercial stage. The key aspect in the molten carbonate electrolysis profitability is the purity of end product in addition to the specific energy consumption of the process. Major aspects affecting the morphology and the purity are electrode materials, electrolyte composition and temperature. Corrosion heavily affects the carbon quality, and it is challenging to reach low-cost stack structure to elevate system voltage in order to limit the current requirement and power supply cost.

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