Electrochemical CO_2 conversion to elementary carbon in binary Li-Ca carbonate

Emma Laasonen[1*], Anafi Nur'Aini[2], Alireza Charmforoushan[3], Vesa Ruuskanen[2], Markku Niemelä[2], Tuomas Koiranen[1], Jero Ahola[2], Jyrki M. Mäkelä[3]

1 School of Engineering Sciences, LUT University, Lappeenranta, Finland;

2 School of Energy Systems, LUT University, Lappeenranta, Finland;

3 Aerosol Physics Laboratory, Faculty of Engineering and Natural Sciences, Tampere University, Tampere, Finland

**Corresponding author: emma.laasonen@lut.fi*

Highlights

- Binary Li-Ca carbonate is suitable for CO_2 conversion to elementary carbon.
- Electrolysis temperature has a significant effect on the product morphology.
- Spherical carbon structures contain the lowest amount of impurities.

1. Introduction

Molten carbonate electrolysis reaction has been proved to be a feasible method to convert CO_2 to elementary carbon. Based on various experimental works published within the last 15 years, including but not limited to [1-7], Li_2CO_3 is the most prominent electrolyte for this application. Besides pure Li_2CO_3, the suitability of various carbonate mixtures has been studied. Based on thermodynamic data and calculated deposition potentials in [8], it can be determined whether carbon or metal is deposited during the electrolysis. Accordingly, the carbonates that could be utilized in carbon production by molten salt electrolysis are Li_2CO_3, $MgCO_3$, $CaCO_3$, $SrCO_3$, and $BaCO_3$. In this study, *an* eutectic mixture of Li2CO3-CaCO3 (80:20 mol%) is employed as the electrolyte. The limited availability of prior research on electrochemical carbon production using this specific electrolyte leaves room for further investigation. The primary focus of this study is to examine the influence of electrolysis temperature on the resulting carbon morphology.

2. Methods

Molten carbonate electrolysis was conducted in Li_2CO_3-$CaCO_3$ (80:20 mol%) electrolyte with Inconel Alloy HX (Harald Pihl) as cathode and anode. Planar electrodes were placed vertically, and the gap between the electrodes was 2cm. According to the manufacture's datasheet the corrosion resistance of the material is high, hence this material selection. Electrode area in molten salt was 50cm^2. Electrolysis time in all the experiments was 90min, and applied constant current was 10A, equivalent to current density of 0.2A/cm^2. Experiments were conducted at temperatures of 700°C, 725°C, 750°C, and 775°C.

Scanning electron microscopy (SEM) was employed to determine carbon morphologies. Additionally, energy-dispersive X-ray spectroscopy (EDX) was used to examine possible metal residues mixed with the carbon. X-ray diffraction (XRD) analysis was utilized to study the graphitization of the carbon product and determining what are the possible impurity compounds present in the sample. Prior to analysis the samples were washed with HCl and rinsed with deionized water to dissolve salts residues from the carbon.

3. Results and discussion

SEM images taken from the carbon produced at different temperatures showed that morphology of the carbon is changing while temperature is increased. The transition is evident from platelet structures to more spherical and tubular formations along increasing temperature. Analysis using EDX revealed the presence of not only carbon but also oxygen, chromium, iron, nickel, molybdenum, and chloride in the samples. Metals originate from the electrodes, while chloride is attributed to residues from the sample washing process.

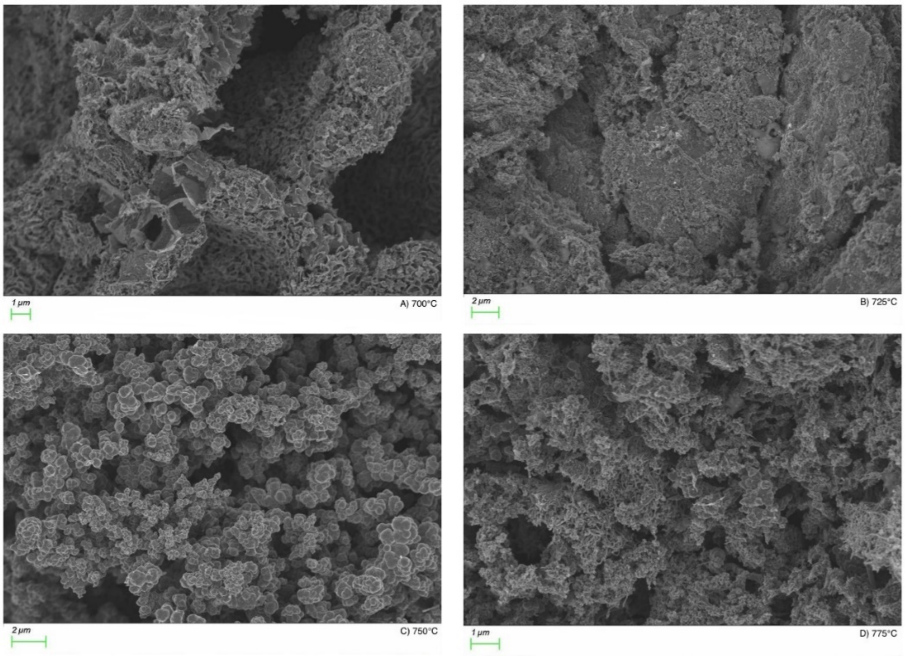

Figure 1. SEM images of the carbon produced at various electrolysis temperatures during a 90min 10A constant current electrolysis. Produced morphologies were A) crystalline particles with platelet-like sharp edges at 700°C, B) crystalline particles with rounded edges at 725°C, C) spherical nano-onios at 750°C, and D) crystalline tubular and spherical structures at 775°C.

XRD findings indicated that the predominant component of the sample is graphitic carbon, but impurities were also detected. The most significant impurities found were $LiCrO_2$, $FeNi_3$, and $Li_6Mo_2O_7$. The quantity of impurities varied among the samples, with the spherical carbon produced at 750°C exhibiting the least amount of impurities.

4. Conclusions

The study findings indicate that eutectic Li-Ca carbonate is a viable option for converting CO_2 to elemental carbon across different temperatures. The temperature during electrolysis plays a crucial role in influencing the product's morphology, highlighting the importance of precise control. The ability to change product morphology by adjusting temperature alone is promising for potential industrial-scale applications, as changing temperature is a more straightforward process compared to changing electrolyte or electrode materials.

References

[1] X. Liu, J. Ren, G. Licht, X. Wang, S. Licht, Adv. Sustain. Syst. 3, 1900056 (2019).
[2] E. Laasonen, V. Ruuskanen, M. Niemelä, T. Koiranen, J. Ahola, J. Environ. Chem. Eng. 10, 106933 (2022).
[3] M. Johnson J. Ren, M. Lefler, G. Licht, J. Vicini, X. Liu, S. Licht. Mater. Today Energy. 5, 230–236 (2017).
[4] J. Ren, F.-F. Li, J. Lau, L. González-Urbina, S. Licht, Nano Lett. 15, 6142–6148 (2015).
[5] E. Laasonen, M. Sorvali, V. Ruuskanen, M. Niemelä, T. Koiranen, J. Ahola, J. M. Mäkelä, T. Joronen. J. CO_2 Util. 69, 102390 (2023).
[6] S. Licht, A. Douglas, J. Ren, R. Carter, M. Lefler, C. L. Pint, ACS Cent. Sci. 2, 162–168 (2016).
[7] X. Liu, X. Wang, G. Licht, S. Licht, J. CO_2 Util. 36, 288–294 (2020).
[8] L. Li, W. Wong-Ng, K. Huang, L. P. Cook, L. P. Cook, Materials and Processes for CO_2 Capture, Conversion, and Sequestration, John Wiley & Sons, 2018.

Keywords
Molten carbonate electrolysis reaction, carbon capture and utilization, electrochemical reduction, electrochemical conversion