Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Electrochemically Induced Crtysallization of Amorphous Materials in Molten $MgCl_2$: Boron Nitride and Hard Carbon

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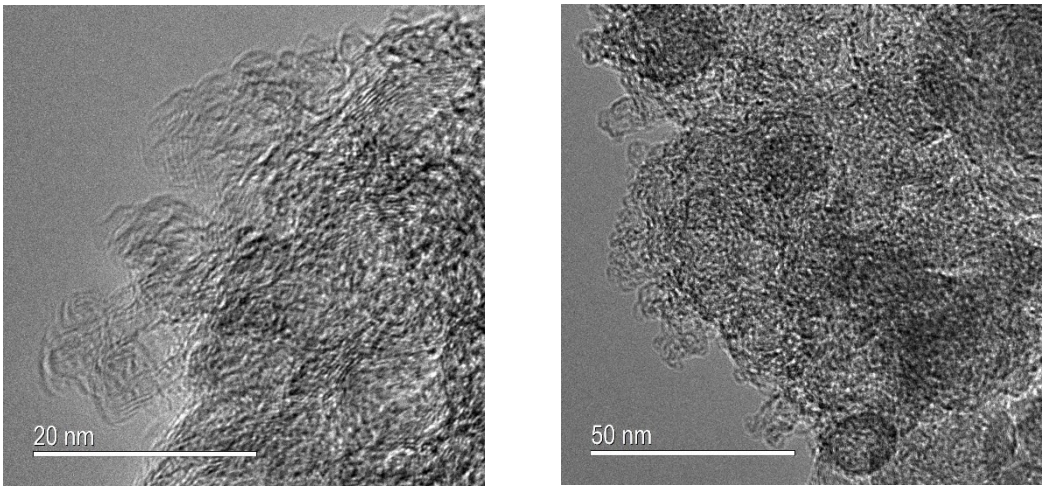


Figure S1: TEM images of hard carbon prior to electrochemical treatment

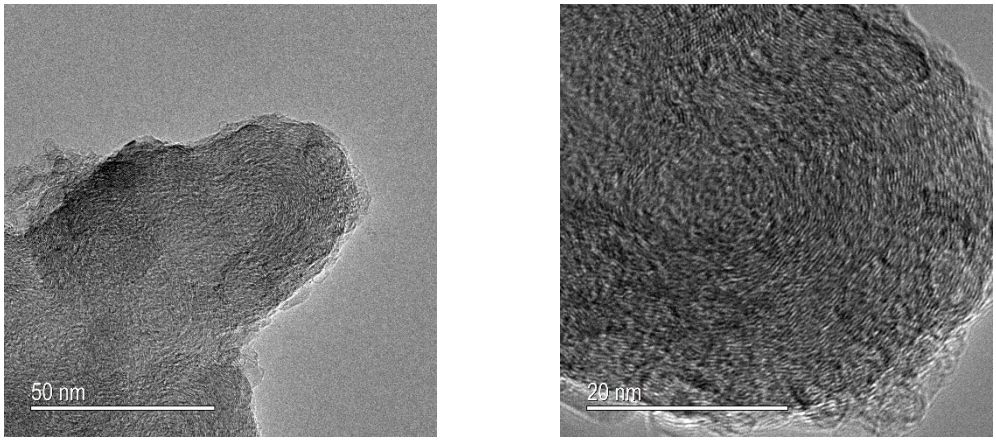


Figure S2: TEM images of EGC post electrochemical treatment in molten $MgCl_2$

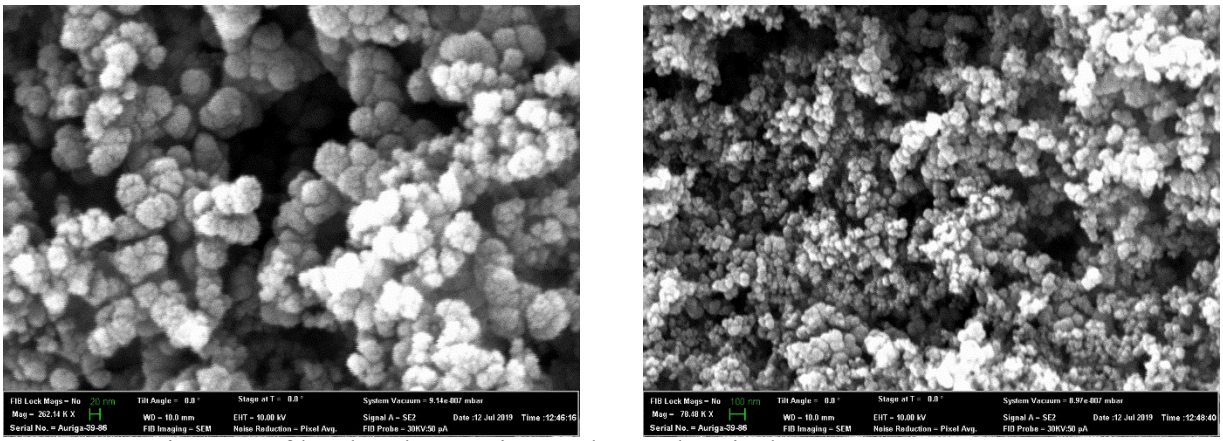


Figure S3: SEM images of hard carbons prior to electrochemical treatment

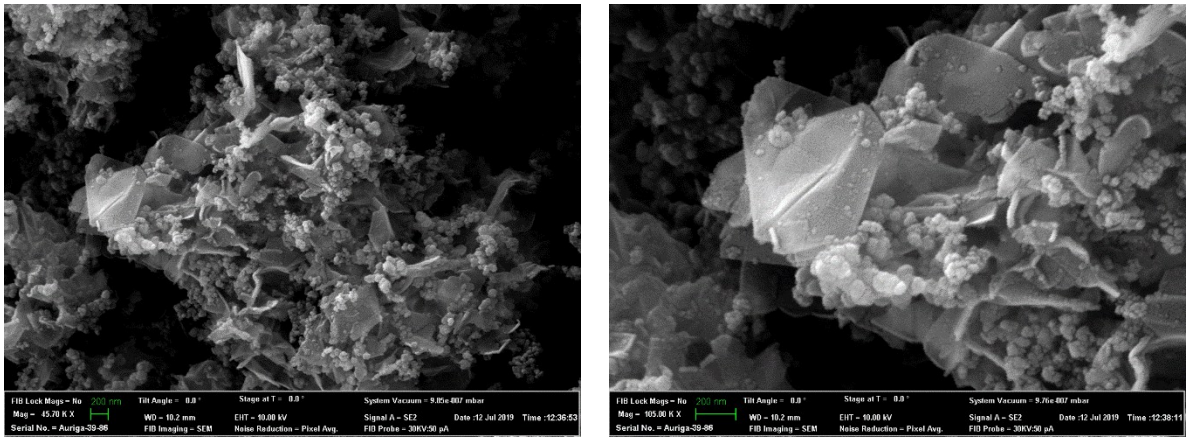


Figure S4: SEM images of EGC psot electrochemical treatment in $MgCl_2$

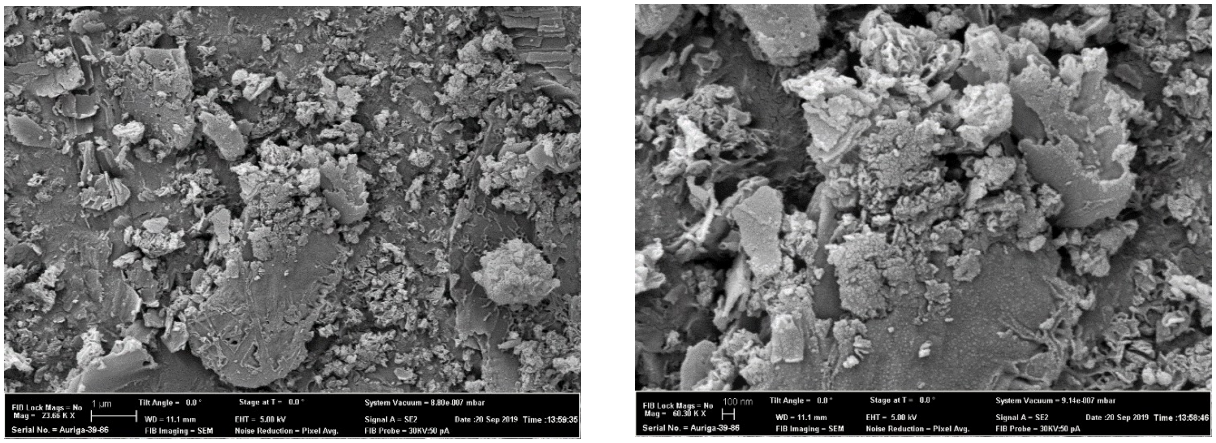
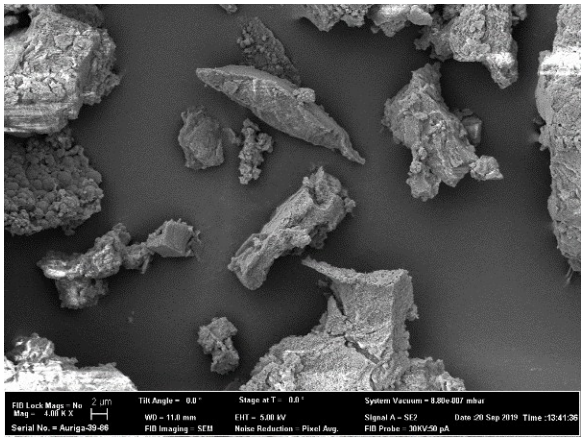


Figure S5: SEM images of amorphous BN prior to electrochemical treatment



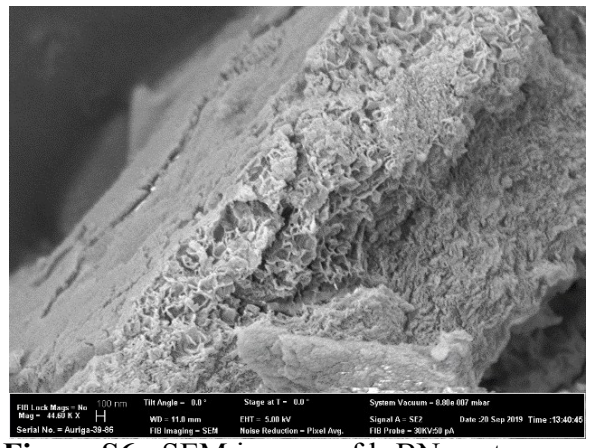
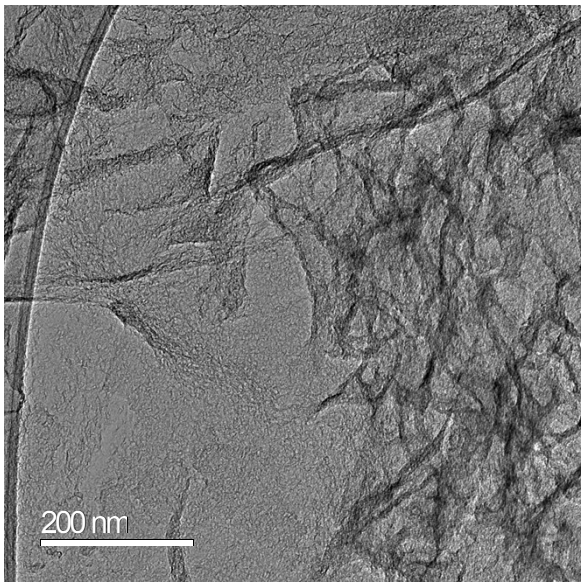


Figure S6: SEM images of h-BN post electrochemical treatment in $MgCl_2$



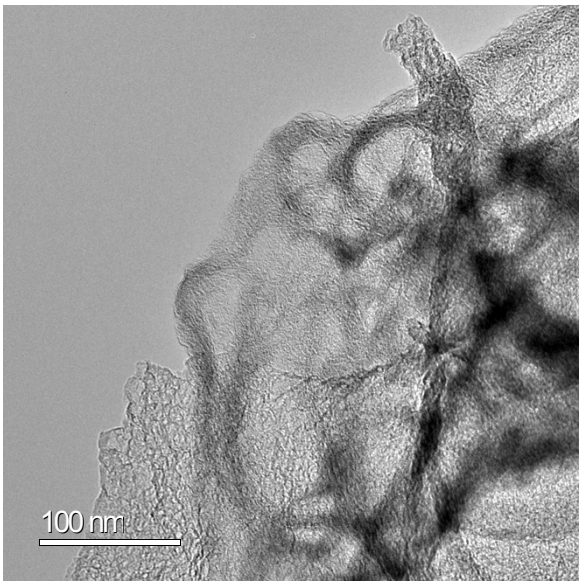


Figure S7: TEM images of amorphous BN prior to electrochemical treatment

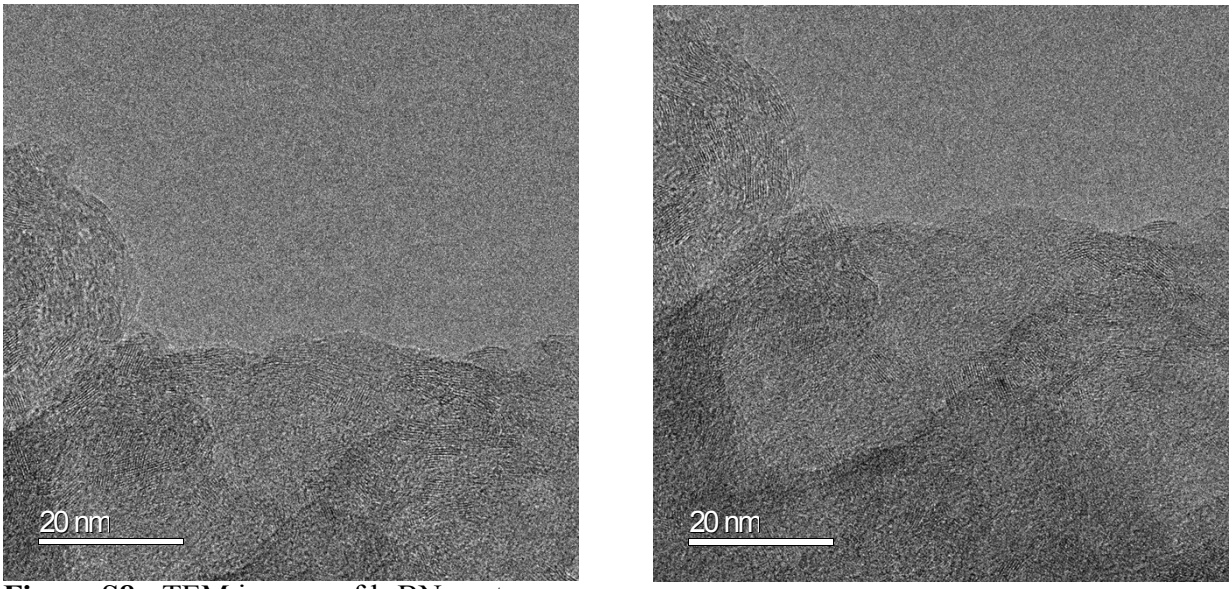


Figure S8: TEM images of h-BN post electrochemical treatment in $MgCl_2$

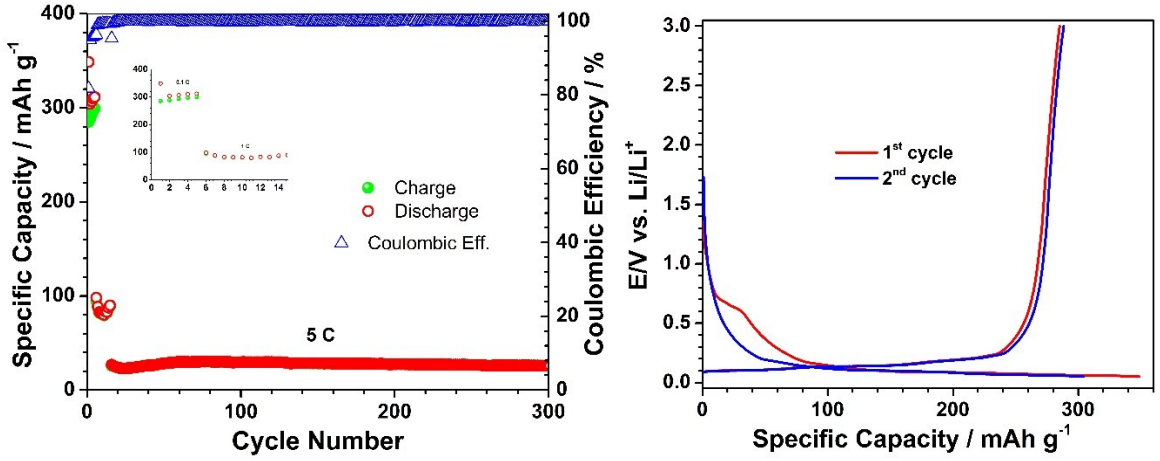


Figure S9: Cycling stability and charge-discharge profiles for commercial synthetic graphite.

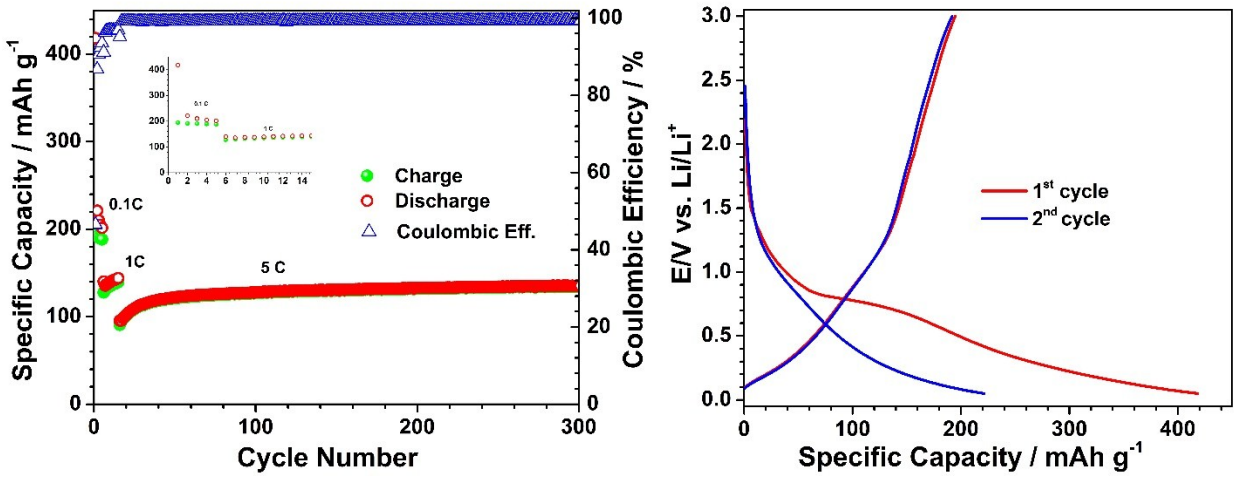


Figure S10: Cycling stability and charge-discharge profiles for hard carbon.

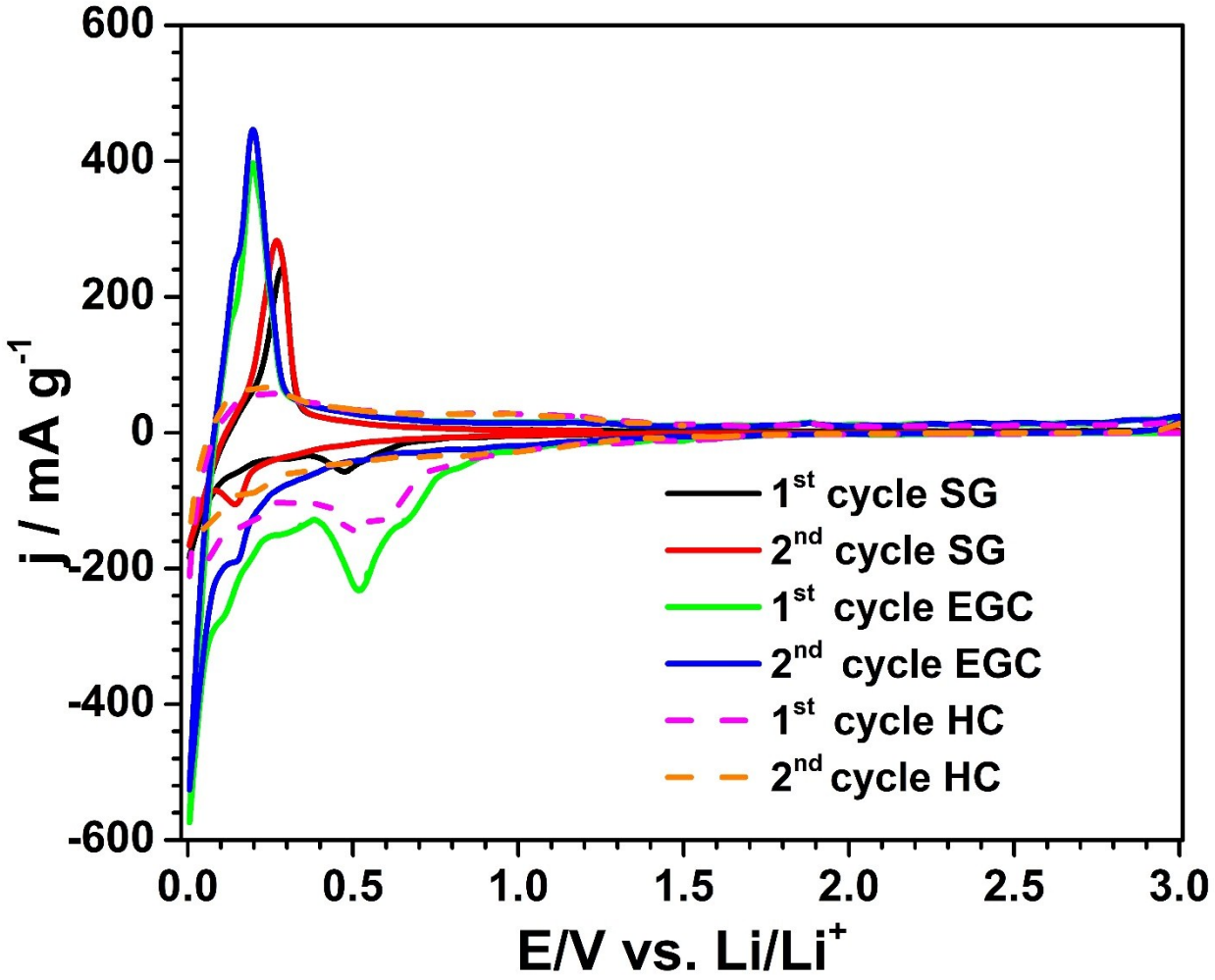


Figure S11: Comparision of cyclic voltammetry of EGC, synthetic graphite, and hard carbon at a scan rate of 0.1 mV s^{-1} vs. Li/Li^+.

$MgCl_2$ Dehydration:

Dehydration of $MgCl_2$, which forms hydrates with up to 12 hydration waters, proceeds with the sequential release of water down to the monohydrate. Upon further heating, the monohydrate hydrolyzes into MgO and HCl[1]. To aid in the dehydration of $MgCl_2$ while preventing hydrolysis, ammonium chloride has been used. When heated in the presence of hydrated $MgCl_2$, ammonium chloride forms a carnallite intermediate that facilitates the release of water[2,3].

$$MgCl_2 \cdot nH_2O + NH_4Cl \rightarrow MgCl_2 + NH_3(g) + HCl(g) + H_2O$$

Commercial anhydrous $MgCl_2$ (Alpha Aesar, 99.9%) was stored in a vacuum oven at 120 °C. 500 g of $MgCl_2$ ·xH2O was weighed and mixed with 250 g of NH_4Cl (Alpha Aesar, 99%). The mixture was then added to a 12-inch long quartz crucible with a 3-inch inner diameter. The crucible was placed in a quartz reactor equipped with a sealed, removable 3-port head. The assembled reactor was placed in a Lindberg Blue tube furnace, and the reactor was purged with UHP Ar (Airgas) for 1 hour. UHP Ar was constantly flowing at 0.5 L/min during the heating and cooling. The salt was heated from room temperature to 400 °C at 20 °C/min and held at this temperature for 2 hours. The salt mixture was then heated to 850 °C at 20 C/min for 1 hour to remove excess ammonium chloride and fuse $MgCl_2$. After 1 hour at 850 °C the furnace was turned off and allowed to cool to room temperature. Once cooled, the reactor was kept under UHP Ar and was transferred into a UHP Ar-blanketed glovebox. The fused $MgCl_2$ salt was retrieved and was broken into smaller pieces. The salt was then stored in Mason jars inside the glovebox before being used for the electrochemical experiments.

Synthesis of BN:

0.05 mol boric acid and 1.2 mol urea were dissolved in deionized water (200 ml). The homogeneous solution was heated to 60 °C for recrystallization. A white powder was obtained by the subsequent evaporation of water. Then the precursors were heated with at $5°C \cdot min^{-1}$ to 900 °C and kept for120 min under N_2 atmosphere.

REFERENCES

1. Skar, R. A. Chemical and Electrochemical Characterization of Oxide/Hydroxide Impurities in the Electrolyte for Magnesium Production. Nnorges Teknisk-Naturvitenskapelige Universitet, 2001.
2. Kipouros, G. J.; Sadoway, D. R. A thermochemical analysis of the production of anhydrous MgCl2. *Journal of Light Metals* **2001**, *1*, 111-117.
3. Dai, Sheng, et al. "Measurement of molten salt Raman spectra by the use of fiber optics." *Microchimica Acta* 108.3-6 (1992): 261-264.