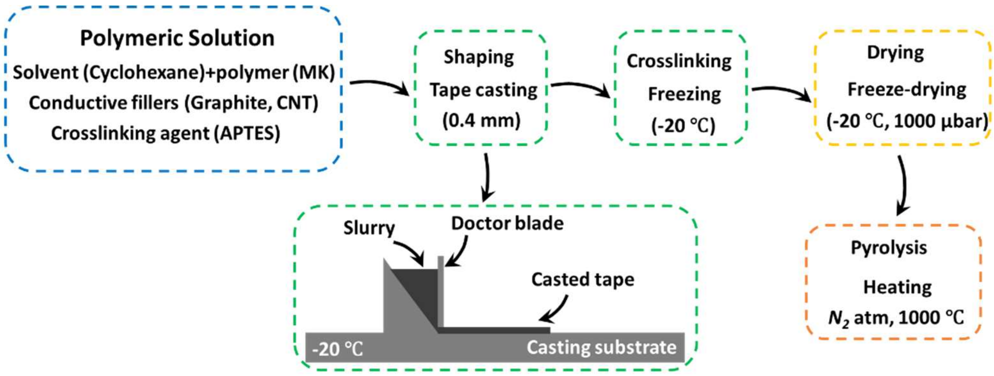
How contact angle measurements help to get insights on how to prolong the cycle life of rechargeable Zinc-Air Batteries

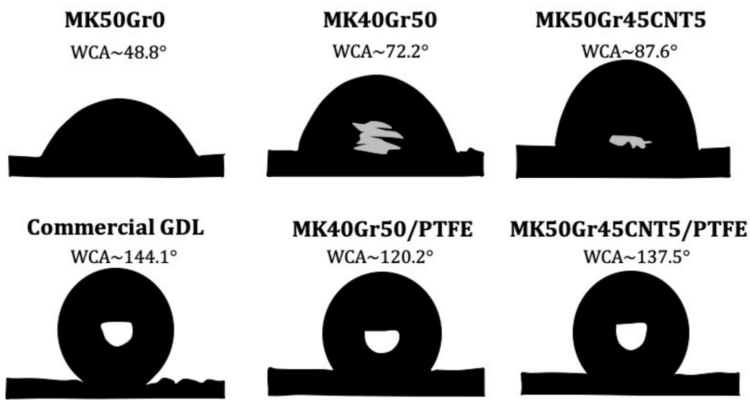
Compared to many other battery types, Zinc-air batteries have a favorable energy density and specific energy (and weight) ratio due to the utilization of air as reactant source. Rechargeable zinc-air batteries have gained considerable attention in the past few years as a promising technology for green energy storage. One of the main open challenges is still to design efficient gas diffusion layers (GDL) to increase the oxygen diffusion rate and the cycle life of metal-air batteries. Generally, GDLs are thin and flat membranes with a porous multi-layered structure. This multilayered structure requires a complex manufacturing process which renders the commercial production of GDLs quite labor intense. To overcome this issue, ongoing research aimed at generating 3D hierarchical porous structures with different shapes and geometries by a combination of freeze casting and tape casting. As material of choice silicon-based polymer-derived ceramics (PDC) is widely used for the fabrication of GDLs due to the tailorable pore size, pore morphology, surface characteristic and electrical conductivity. Recently, by applying the freeze tape casting technique, Wilhelm and coworkers have developed a novel porous conductive ceramic membrane with high hydrophobicity as cathodic GDL for zinc-air batteries that significantly enhanced the cycle life.

In this work, the authors first fabricated the bilayer structure with a thickness of 390 µm and an open porosity of 55%, and then introduced conductive fillers (graphite and carbon nanotubes) as well as a superhydrophobic coating (polytetrafluoroethylene (PTFE)) to improve the electrical conductivity and hydrophobicity, respectively. The ceramic GDL is manufactured by using the freeze tape casting method as shown in **Picture 1**. Preceramic polymer was first dissolved in cyclohexane followed by addition of a crosslinking agent and a conductive filler. After tape casting, the cast membrane was freeze-dried and pyrolyzed to obtain the final porous membrane.



Picture 1: *Preparation process of ceramic gas-diffusion layer by freeze tape casting method.*

To study the surface properties of GDLs, they conducted contact angles measurements with an optical contour analysis system OCA (DataPhysics Instruments, Germany). As shown in **Picture 2**, the addition of fillers made the surface more hydrophobic (~72.2°, ~87.6°), while the bare ceramic GDL showed a hydrophilic surface (~48.8°). Coating the GDLs with PTFE led to hydrophobic surface (~120.2°, ~137.5°), which can reach similar levels like the commercial one with water contact angle of ~144.1°. The porosity of the new GDLs could reach up to 55%, which was even higher than the commercial GDL (50-52%).



Picture 2: *Water contact angles of various ceramic samples*

Table 1: *Typical properties of ceramic gas-diffusion along with zinc-air batteries performance*

GDL*	Hydrophobic behavior (WCA) (°)	Zinc-air batteries performance (after 200 cycles)
MK50Gr50/PTFE	120.2	Specific capacity 625 mAh g^{-1}, 60% round-trip efficiency
MK50Gr45CNT5/PTFE	137.5	Specific capacity 570 mAh g^{-1}, 67% round-trip efficiency
Commercial GDL	144.1	Specific capacity 542 mAh g^{-1}, 66% round-trip efficiency

* Pt-Ru/C was employed as cathode catalyst for zinc-air batteries

The performance of the new GDLs in zinc-air batteries was evaluated by conducting galvanostatic discharge-charge measurements (**Table 1**). Especially the PTFE coated GDL MK40Gr50/PTFE was able to breathe in longer, discharged over 48 h, and possessed a higher specific capacity (625 mAh g^{-1}) than the commercial GDL (542 mAh g^{-1}). Due to the symmetric sponge-like structure, the ceramic GDLs possessed also an improved oxygen exchange rate and shorter pathways for oxygen ion-/electron kinetics, and thus displayed an outstanding cycle life of over 200 cycles and complete discharge over 48 h, outperforming the commercial GDL. Moreover, the ceramic GDLs displayed no morphological changes even after 200 cycles due to the highly aligned bilayer structure on the superhydrophobic surface. MK40Gr50/PTFE and MK50Gr45CNT5/PTFE ceramic GDLs possessed the highest reported capacity, operating potential and reversibility until now. The right combination of porosity, conductivity, and hydrophobicity all played major roles to get excellent GDLs in improving the zinc-air batteries performance.

In summary, the authors fabricated new ceramic GDLs by using a much easier manufacturing process compared to the commercial one—the special freeze tape casting technique. The porosity, conductivity and hydrophobicity of the ceramic GDLs were greatly improved by introducing conductive fillers (graphite and carbon nanotubes) and a hydrophobic coating (polytetrafluoroethylene (PTFE)). This work sheds light on designing 3D hierarchical porous ceramic GDLs with excellent zinc-air batteries performance to compete with the commercial GDLs in the future.

An optical contour analysis system OCA (DataPhysics Instruments GmbH, Germany) was used in this research.

For more information, please refer to the following article:

A new silicon oxycarbide based gas diffusion layer for zinc-air batteries; Prabu Moni, Amanda Deschamps, Daniel Schumacher, Kurosch Rezwan, Michaela Wilhelm; *Journal of Colloid and Interface Science* **2020***,* 577, 494-502; DOI: 10.1016/j.jcis.2020.05.041