c-VACNT™, New Nano-to-Macro Material Platform with a Rich Application Potential

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ABSTRACT

c-VACNT™ - structures are made with a combination of non-proprietary and proprietary manufacturing process steps including photolithographic patterning of catalyst wafers, VACNT growth, carbon infiltration, separation from a growth substrate, optional secondary coating and/or other local or global surface modifications. The c-VACNT™ material of which these structures are made of has a nano-carbon based bi-continuous phase structure with 20-100 nm wide slit pores that are mechanically stable despite being semi-flexible so that they can survive drying after soaking in acetone or water soaking. They presently can be up to 5 mm tall and have features and/or through channels, notches, branches, arms as well as internal or external shapes ranging in size from 5 μm to over 100 mm.

We present here examples of selected fluid reactor applications demonstrating how these c-VACNT™ structures can be used to significantly improve the performance of medical and industrial devices, including extracorporeal membrane oxygenators (ECMOs) and artificial lungs.

Keywords: c-VACNT™ - structures, c-VACNT™ - RCE, ECMO, artificial lung

c-VACNT™ - MATERIAL

The c-VACNT™ material [1] in its native form is a pure nanocarbon based porous material comprised of nanocarbon ligaments that are "spot-welded" together by a thin carbon film of thickness T wherever the original nanocarbon based ligaments are at a distance $D \leq 2*T$, i.e., touch or nearly touch each other. Typically, $T = 2 - 30\ nm$, but lower or higher values can also be achieved with process tuning. This results in the creation of a mechanically robust open-pore cellular network material with a bi-continuous tortuous phase structure. The carbon-based spot-welding process gives the material sufficient mechanical rigidity so that it can survive fluid exposure and subsequent drying, even if the liquid is acetone, while still being overall somewhat mechanically flexible. One of the possible and volume scalable implementations of the new material platform uses vertically aligned carbon nanotubes (VACNTs) as ligaments.

Figure 1 depicts the carbon "spot-welding" process that gives the c-VACNT™ material its tunable strength (controlled by the ligament strength and the film thickness T which also controls the spatial frequency of these joints). Figure 2 shows an SEM image of the nanostructure of a native type c-VACNT™ material with $T \approx 8 - 12\ nm$ when CNTs are used as ligaments resulting in an average coated ligament diameter of $d \approx 20\text{-}25\ nm$, a bi-continuous phase structure with slit pores (≈ 20-100 nm x 200-1000 nm), a solid carbon volume density of ≈ 8 % and a void space of 92%. The strength, density, and thus the void phase of this material can be tuned by the thickness T and the volume density of its ligaments. Figure 2 also shows the tortuous nanostructure of this material.

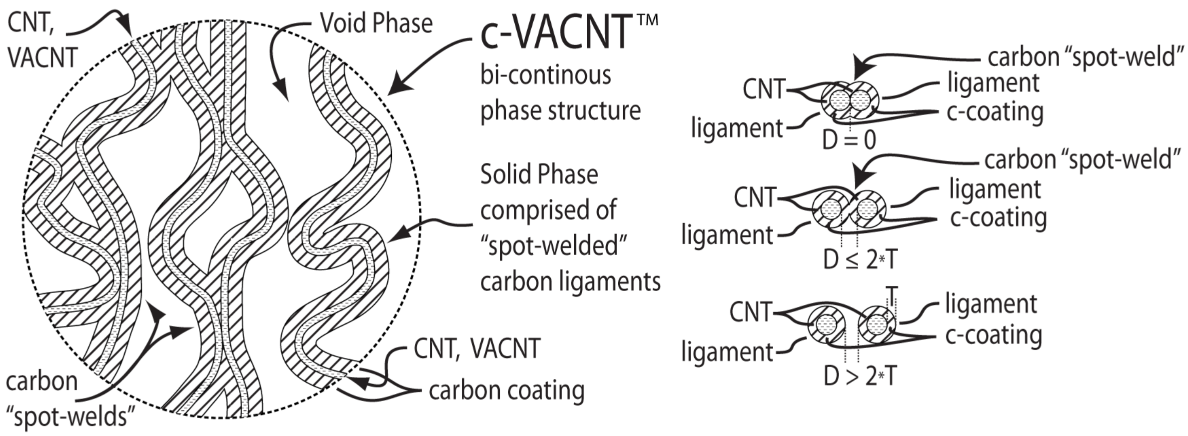

Figure 1: c-VACNT™ carbon "spot-welding" process

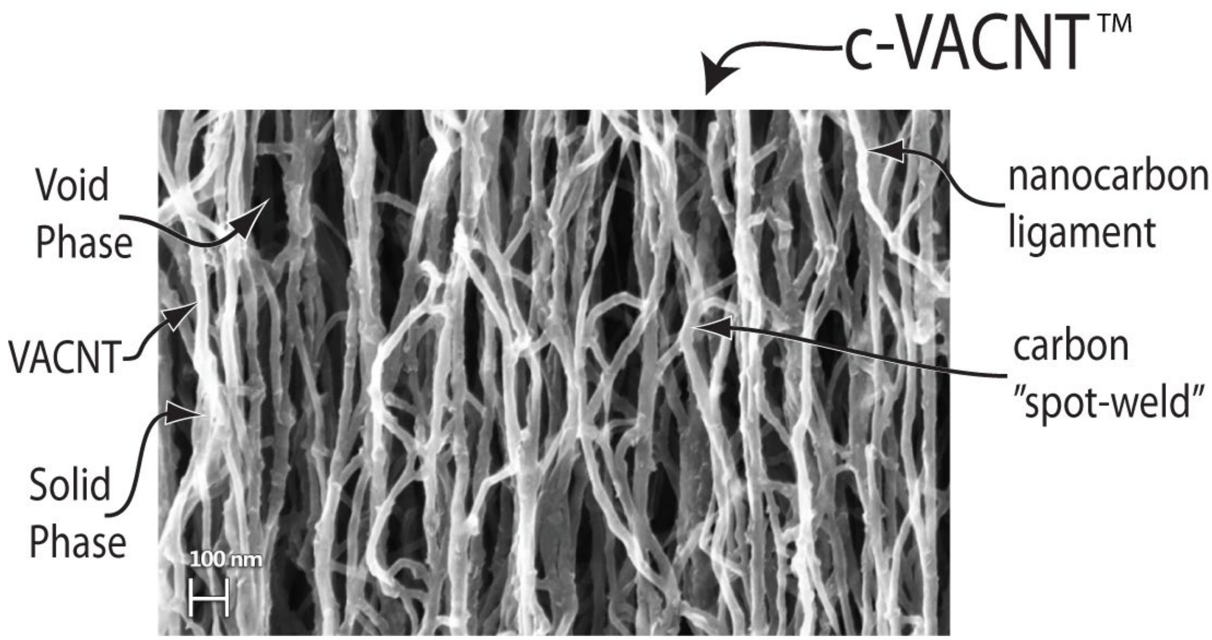

Figure 2: c-VACNT™ material tortuous nanostructure using VACNT's as nanocarbon ligaments

The spacing of the ligaments is about 80-200 nm for the material sample of Figure 2. Therefore, it mechanically stops particles of > 200 nm size from penetrating its structure, thereby having a natural nano-porous filtering functionality. Note that this pore spacing is about the same order of magnitude as the average collision distance between gas molecules at atmospheric pressure. Therefore, gas or liquid transmission through such material, while still possible, will experience a notable pressure drop (following Darcy–Forchheimer law when diffusion can be ignored). Figure 3 shows the pressure drop for forced nitrogen flow through a material similar to the one in Figure 2. Even, when no force is applied to a fluid surrounding such (≈ 92%) highly open nano-porous material liquids, dissolved or suspended solids or quasi-solids (salts, small organic or biological materials, etc.), nano-sized particles, polymers, vapors and gases can still flow through them when driven by a concentration gradient, thereby exhibiting a membrane like function where different material flow through it at different rates, thus providing separation and isolation functionalities (Fick's law, Graham's law).

The solid phase of this material can be further modified by providing a second coating, preferably a conformal coating to either enhance or prevent liquids from penetrating this nano-porous structure. For example, a hydrophilic coating will enhance liquid penetration while a hydrophobic coating can result in stopping liquid from entering such a structure (up to a certain pressure), so that only gases and/or vapor can travel through, providing functionalities for example, that a membrane desalination system could take advantage of.

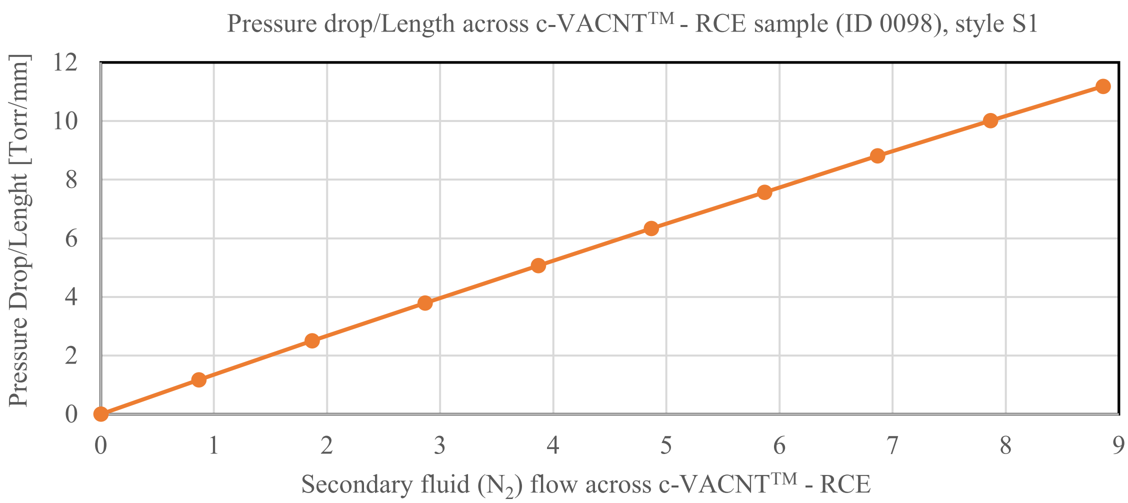

Figure 3: Pressure drop/Length for forced secondary fluid N_2 gas flow through an open pore cellular network c-VACNT™ - material as shown in Figure 2

The height η of a liquid inside the capillary column having a diameter δ is defined by the force equilibrium between the weight of the column and the support from the surface tension. This leads to the formula where γ represents the surface tension of the liquid, ρ the liquid's density, Θ the liquids contact angle and g = 9.80655 m/s^2 is the acceleration due to gravity.

$$\eta = \frac{4 * \gamma * cos(\Theta)}{\delta * \rho * g} \tag{1}$$

As can be seen in equation (1), the height η is positive for hydrophilic conditions, i.e. $\Theta < 90°$ and negative for hydrophobic conditions, i.e. $\Theta > 90°$. Therefore, for hydrophilic conditions, the liquid gets sucked into the capillary and for hydrophobic conditions is repelled from it, thus providing a barrier for liquid entry. The smaller the diameter δ and liquid density ρ the bigger is this suction/repulsion effect. With the average coated ligaments having a spacing of ≈ 80-100 nm and covering typically < *25%* of a given external surface additional liquid repellent effects (see lotus leaf) can apply (Cassie-Baxter state) for the case of a hydrophobic coated c-VACNT™ material. With an appropriated hydrophobic coating material selection and a correctly chosen hydrophobic coating process, we were able to transform uncoated c-VACNT™ material that was hydrophilic into a material with superhydrophobic (contact angle ≥ *150°)* properties that maintain its liquid repellent properties for over a month. Figure 4 shows the change in contact angle for an uncoated and hydrophilic coated c-VACNT™ material transforming it due to its nanostructure into a superhydrophobic material. When a diameter *δ = 200 nm* is used in equation 1 (upper diameter of slit pore width) for water at a temperature of 25 °C we find that the superhydrophobic repellant force (for a material with a 150° contact angle) is > 180 PSI, i.e., this is the amount of fluid pressure needed to overcome to be able to enter a dry c-VACNT material. The c-VACNT™ material shown in Figure 2 has been tested to withstand > 30 PSI pressure, and its strength can be further tuned. The time-dependent variation of the contact angle measurement for the hydrophobic coated c-VACNT™ material is also shown in Fig.4 for a material that has been constantly submerged in water and stayed dry.

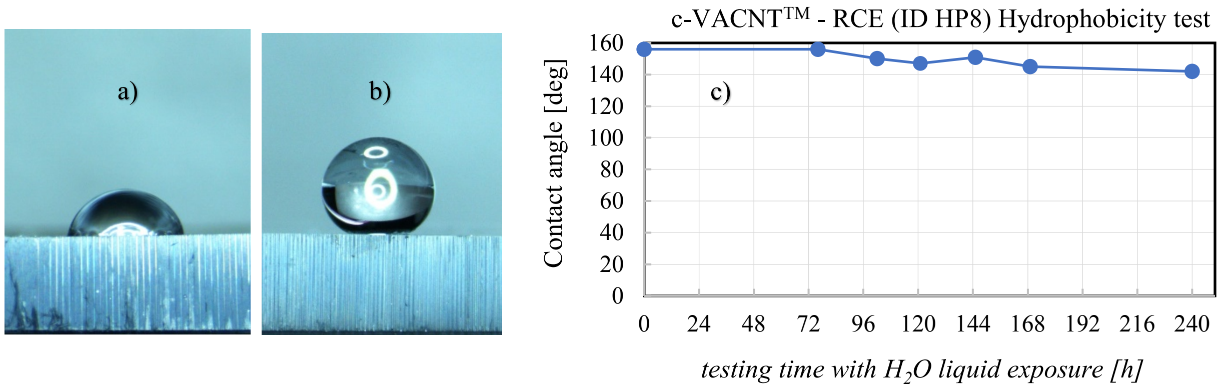

Figure 4: Contact angle for a) native (70°) and b) superhydrophobic coated (>150°) c-VACNT™ material and c) time-dependent contact angle when submerged in water for an extended time

When needed, these various functional material properties can be used as an advantage to keep particles (red blood cells, etc.) and even liquids out of its porous structure and thereby impart a selective transmission functionality. By properly structuring the c-VACNT™ material, the building of novel fluid reactors [1] will thus be enabled, among other applications.

c-VACNT™ STRUCTURES

For example, by using photolithographic patterned catalyst wafers, VACNTs can be grown on a substrate in a first chemical vapor deposition (CVD) based process step. The carbon coating providing the localized "spot-welding" can then be applied onto the same wafer with a different CVD process, thus transforming the VACNT-wafer into a c-VACNT™ precursor wafer. After the c-VACNT™ precursor growth process, the resulting c-VACNT™ precursor structures are separated from their growth wafers and further processed as needed with various proprietary and nonproprietary process steps thus becoming application specific, free-standing c-VACNT™ - structures [1] that can be integrated into their targeted products.

The c-VACNT™ - structure production capability developed in our CVD Application Laboratories enables the manufacturing of a wide variety of c-VACNT™ structures with the change of the photolithographic mask and as needed CVD process tuning for different customer requirements. With auxiliary secondary process steps (for example laser 3D sculpting) additional functionalities and features can be imparted. Figure 5 shows a range of different free-standing, 2mm tall, native VACNT™ - structures that can, as discussed above, be further modified to more optimally fit a particular application. Table 1 gives more details of the different c-VACNT™ structure sample type *ST1-ST12* with each c-VACNT™ structure tuned for both high porosity and sufficient strength to survive to dry after getting wet with water or even acetone.

Both the VACNT growth and the carbon infiltration process used to build such and other c-VACNT™ structures have been implemented, for example, on a Carbon+™ 100 System (Figure 6) resulting in a processing capacity of over 90 - 100mm catalyst wafers /week.

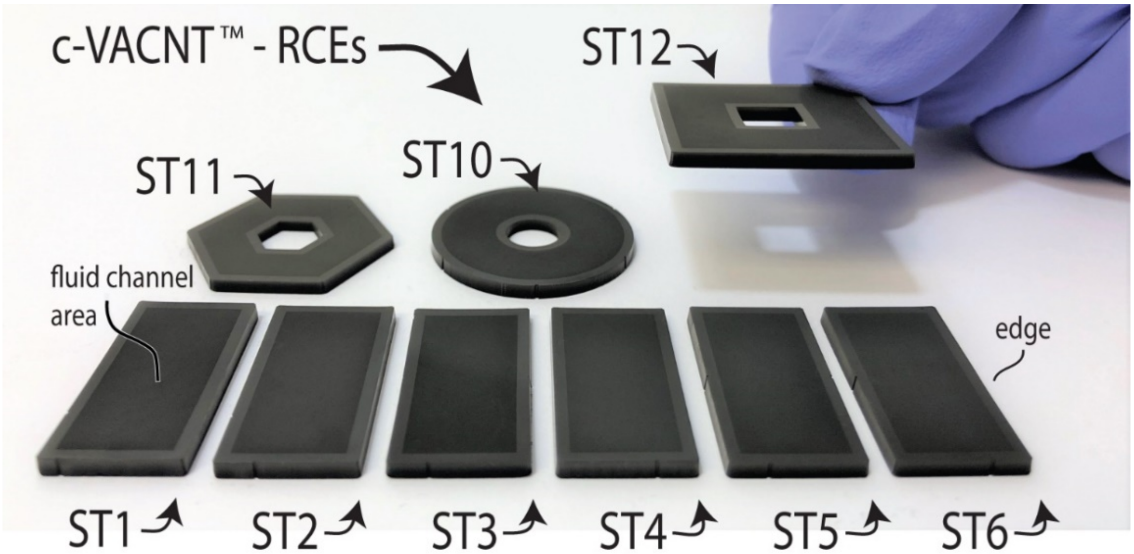

Figure 5: A range of c-VACNT™ - structure types (Table1)

Figure 6: c-VACNT™ precursor structure manufacturing tool

c-VACNT™ - RCEs

Reactor core elements (RCEs) are components used to build three or four port fluid reactors [1,2] which are then used to compositionally change at least one primary input fluid into a primary output fluid with the aid of one secondary fluid or one secondary input and output fluid. Typically, the primary fluids are liquids, and the secondary fluid (or fluids) is (are) either a gas or liquid. Typical liquids of interest can be biological, pure liquids, liquids with dissolved matter (gases, salts, or solvable liquids), liquids with suspended matter, chemical processing liquids, pharmaceutical liquids, bioreactor related liquids, etc.

The respective fluids processing is done with the aid of a “membrane-like” fluid interface which has a surface area S and an asymmetric transmission function for the secondary fluid (fluids) and at least one key component of the primary input fluid. As discussed above, the c-VACNT™ material has a native membrane-like property at its surface which can then be further enhanced with an additional coating(s) of the ligaments forming the porous c-VACNT™ material and/or by additionally covering all primary fluid accessible surfaces of this material with a thin membrane film, thereby supporting it mechanically on a *100 nm* level with its nano-porous structure. Thus, to get more active “membrane-area,” more surface area needs to be created. This can be accomplished by making [1] many parallel straight and non-tortuous, perforations through this material. These perforations are called fluid channel hereinafter through which the primary fluids travel through the c-VACNT – RCE and they have a surface area $SA_{FC} = \pi*\phi*h$, with ϕ representing the diameter of the channel and h its height. A gap g represents the smallest c-VACNT™ material thickness between two neighboring fluid channels. Any secondary fluid travels through the porous c-VACNT™ material between fluid channel sidewalls and the exterior sides of respective c-VACNT™ -RCE and a respective secondary fluid entrance or exit port. The sidewall of each fluid channels effectively functions as a membrane with an asymmetric transmission that spatially isolates the primary and secondary fluid pathways.

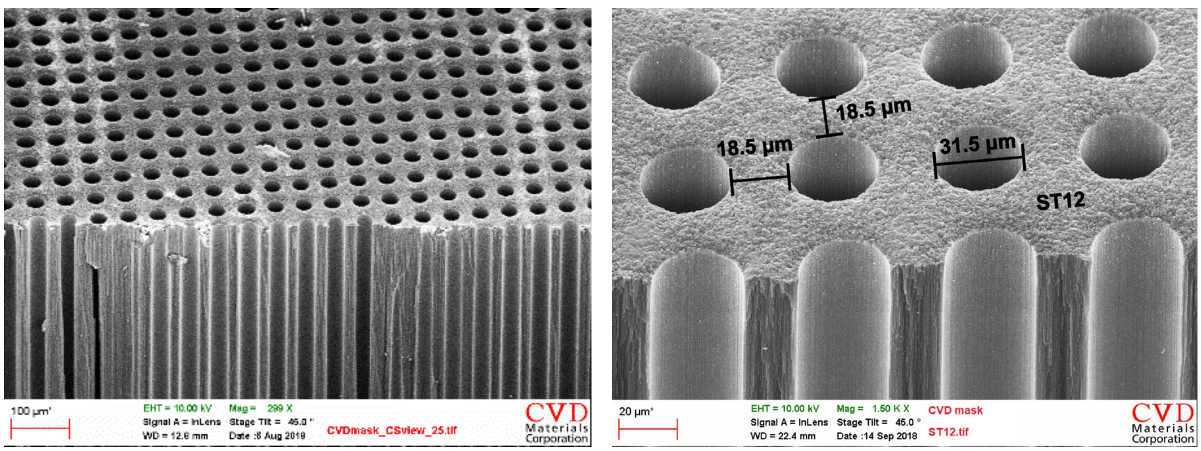

Figure 7: c-VACNT™-RCE with a non-tortuous flow path

Type	ϕ [µm]	*g* [µm]	*N*	*SA* [cm^2]	ρ [%]	***S/V* [m^2/m^3]**
ST1	46.5	18.5	89K	260	34	**29K**
ST2	36.5	18.5	124K	284	29	**32K**
ST3	26.5	18.5	185K	308	23	**34K**
ST4	21.5	18.5	235K	317	19	**35K**
ST5	16.5	18.5	304K	317	15	**35K**
ST6	11.5	18.5	416K	309	10	**33K**
ST10	41.5	18.5	153K	399	29	**28K**
ST11	31.5	28.5	195K	386	26	**33K**
ST12	31.5	18.5	281K	556	24	**31K**
ST20	10.0	10.0	936K	588	16	**65K**
ST21	5.0	5.0	3.7M	1,176	16	**131K**

Table 2: c-VACNT™-RCE key parameters and S/V values for samples shown in Figure 5

Figure 7 shows two differently magnified SEM images of a top and cross-sectional view of the fluid channel area of a cleaved *ST12* type sample having a periodically arranged fluid channel layout with uniform spacing. Table 1 lists key parameters of all the c-VACNT™ - RCE sample types *ST1-ST12* shown in Figure 5 demonstrating that c-VACNT™ - RCEs with fluid channel diameters and gaps of $\phi, g \geq 5\ \mu m$ are already manufacturable in volume. *N* is the number of fluid channel per RCE, ρ represents the ratio of active fluid channel area to total component cross-sectional area, and *S/V* represents the ratio of total available sidewall surface area *S* (membrane area) to component volume *V*. The samples *ST1-ST12* in Figure 5 have a fluid channel area surrounded by an edge exclusion zone with width $\varepsilon = 1.5\ mm$. The samples ST1 - ST6 have a width $W = 15\ mm$ and a length $L = 30\ mm$ and the larger samples *ST10 – ST12* have the narrowest width $W = 30\ mm$ and an inside cutout with a minimum width of *8 mm*. c-VACNT™ structures with $\varepsilon = 0.5\ mm$ or $\varepsilon = 0\ mm$ and/or with larger or smaller *W* or *L* area are also manufacturable.

c-VACNT™ Fluid Reactors

Traditionally high-performance fluid reactors use porous hollow fiber as respective RCE to build their respective reactor cores. Reference [2] discusses in greater detail that the S/V values for the c-VACNT™ - RCEs described in Table 1 can be > 10X than for hollow fiber based reactor cores. c-VACNT™ - RCEs, therefore, can become key components for designing and building high performance reactor cores for next generation fluid reactors for at least selected performance challenged applications.

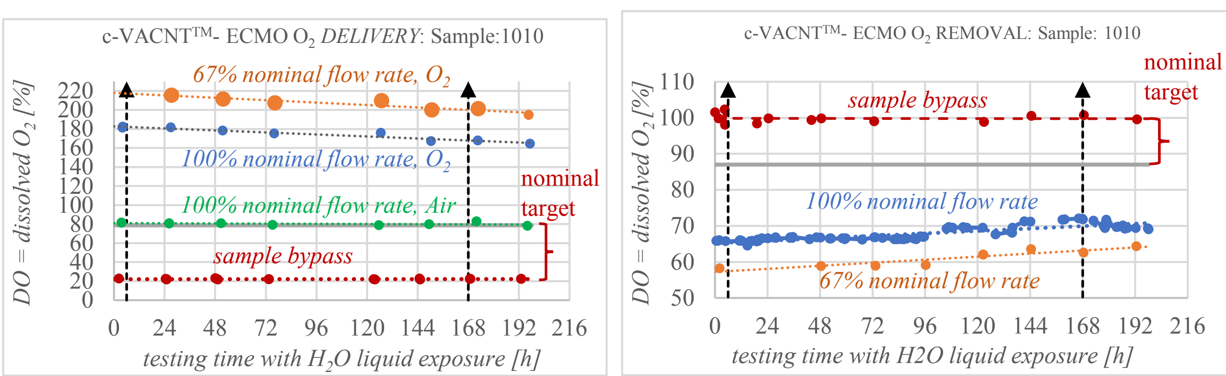

Figure 8: Oxidation/de-oxygenation rate test for hydrophobic c-VACNT™ - ECMO prototypes

c-VACNT™ - ECMOs

One such performance challenged application for fluid reactors using hollow fibers for the last decades are extracorporeal membrane oxygenation devices (ECMOs) used typically for up to 6 hours during cardiopulmonary bypass surgery or for weeks when they are used on prenatal babies. The primary performance challenges are 1) reduction of priming volume (hemodilution), 2) reduction of red blood cell rupture (hemolysis), 3) pressure drop and 4) plasma leakage reducing the oxygen/carbon dioxide delivery/removal efficiency of such devices over time. Therefore different hollow fibers RCEs are used for short and longer term use. Some of these performance issues can be overcome with frequent doner blood/drug injections, which can lead to additional complications. Thus, ECMO use, while saving lives in the short term, can lead to some reduction in quality of life for up to 10 percent of the ECMO treated patients. Hydrophobic c-VACNT™ - RCEs, if they can be made sufficiently blood compatible, therefore provide the potential to significantly improve the performance of ECMO devices by reducing the priming volume 3-6X, by totally eliminating the tortuous path for the blood flow (see Figure 7) and by reducing performance degradation over time (significant reduced plasma leakage). Oxygenation/De-oxygenation rate lifetime test based on ISO 7199 test [3, 4] where H_2O is used as a blood substitute for ECMO prototype devices incorporating superhydrophobic c-VACNT™ - RCE samples have already shown (Figure 8) that they can perform above a specified oxygen delivery and removal (carbon dioxide simulation) rate for more than one week, thus making hydrophobic c-VACNT™ - RCEs, a promising research candidate for next-generation higher performance ECMO product developments. Figure 8 shows (with 6 hours and 7 day markers) test data for water as the primary fluid while monitoring the change in oxygenation and de-oxygenation rate over time. In all cases, the nominal performance rating is exceeded during the test time, both for gas delivery and removal and with both O_2 or Air as the sweep-gas. The nominal flow rate for Air compared to O_2 is > 13%.

c-VACNT™ artificial lung

Reference [3] describes how the > 10X higher S/V ratio of c-VACNT™ - RCEs can also be used to design portable ECMOs that are so much more efficient that they can use air (delivered by an air pump) as sweep gas (instead of using 100% Oxygen delivered from a high pressure tank). In addition, the pressure drop of such a c-VACNT™ - ECMO device can be designed to be low enough that a reasonably healthy human heart can power it. This decrease in pressure drop across the device could potentially eliminate the need for a blood pump, which also contributes to the loss of red blood cells (hemolysis)and therefore increases the risk for a reduction of quality of life after temporary use as an artificial lung. Thus, truly portable artificial lungs that give patients with a temporary or permanent lung deficiency an improved quality of life for extended periods of time are feasible. For example, blood oxygenation for premature babies who need time to grow sufficiently strong to breathe on their own or patients awaiting a lung transplant may now be within reach, if the bio-compatibility issue can be successfully resolved.

CONCLUSIONS

We presented here novel nanomaterial (c-VACNT™) that can be used to make freestanding macroscopic structures with a range of tunable functionalities of sufficient strength to handle liquid fluid processing over time. One important application of this material is to make c-VANT™ - RCEs which can be optimized for specific fluid reactor applications. Typically they have 5X – 15X the membrane surface area/element volume ratio compared to hollow fiber based reactor cores and thereby enable the design and manufacturing of a range of higher performance fluid reactors, including ECMOs and even a portable artificial lung that uses air as a sweep gas. Comparing 6-hour use 1.5/7 L/min blood flow rated hollow fibers based ECMOs with c-VACNT™ – ECMOs a 3-6/7-12X priming volume reduction look achievable combined with potentially significantly hemolysis reduction and longer use time, to provide an improved quality of life after an ECMO procedure. Given their inherent higher performance capability, new products can also be enabled.

REFERENCES

[1] US Pat. Application 62754375, Fluid Reactors

[2] K.S., S.G., A.K., A.K., "c-VACNT™ enabled Fluid Reactor Innovations," Techconnect 2019

[3] K.S., S.G., A.K, A.K., Air Powered Artificial Lungs and other High Efficiency Fluid Reactors Innovations, Techconnect 2019

[4] US Pat. Application, 62/839,026, "Testing of Extracorporeal Membrane Oxygenators and other Fluid Reactors"