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## **Semi-solid lithium/oxygen flow battery: An emerging, high-energy technology**

Francesca Soavi<sup>1,2,3,4\*</sup>, Alessandro Brilloni<sup>1,2,3,4</sup>, Francesca De Giorgio<sup>3,4,5</sup>, Federico Poli<sup>1,2,3,4</sup>

<sup>1</sup>*Department of Chemistry “Giacomo Ciamician”, Alma Mater Studiorum Università di Bologna,  
Via Selmi 2, Bologna 40126, Italy*

<sup>2</sup>*ENERCube, Centro Ricerche Energia, Ambiente e Mare, Centro Interdipartimentale per la  
Ricerca Industriale Fonti Rinnovabili, Ambiente, Mare ed Energia (CIRI -FRAME), - Alma Mater  
Studiorum University of Bologna, Viale Ciro Menotti, 48, 48122 Marina di Ravenna RA (RA)*

<sup>3</sup>*BATTERY Srl, Via C. Pisacane 56, Massafra 74016, Italy*

<sup>4</sup>*National Reference Center for Electrochemical Energy Storage (GISEL) - INSTM, Via G. Giusti  
9, 50121 Firenze (Italy)*

<sup>5</sup>*Consiglio Nazionale delle Ricerche, Istituto per lo Studio dei Materiali Nanostrutturati (CNR-  
ISMN), via Piero Gobetti 101, Bologna, 40129, Italy*

\*Corresponding author: francesca.soavi@unibo.it

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### **Highlights**

- Lithium-air batteries (LAB) are one of the most promising next-generation batteries for their high theoretical energy density.
- In semi-solid redox flow batteries, suspended active material particles allow overcoming the solubility limit of redox flow batteries (RFB).
- Semi-Solid Li/O<sub>2</sub> Flow Batteries combine the advantages of high specific energy of LAB and the design flexibility of RFB.

## Abstract

*Lithium-Air (O<sub>2</sub>) batteries are considered one of the next-generation battery technologies, due to their very high specific energy. In parallel, Redox Flow Batteries (RFBs) are getting much attention for energy transition because of their highly flexible design that enables the decoupling of energy and power. However, commercial RFBs still suffer from low energy density. One of the solutions proposed to increase the energy density is the combination of the high energy density of the Li/O<sub>2</sub> battery with the flexible and scalable architecture of redox flow batteries in semi-solid flow Li/O<sub>2</sub> batteries. The challenging activities to develop materials and components, and to prototype semi-solid flow Li/O<sub>2</sub> batteries are here presented and discussed.*

## 1. Introduction: From air breathing to semisolid Li/O<sub>2</sub> cells

Metal-Air (Oxygen) batteries (MABs) have the advantage of using the lightest cathode material available in nature: Oxygen. Since the O<sub>2</sub> is not stored inside the cell but is continuously supplied from the air, the cell capacity is not limited by depleting or amount of cathode active material. The combination of a metal anode and an O<sub>2</sub>-cathode enables to reach extremely high theoretical energy density (Wh/L) that are about 2–10 folds higher than that of today's lithium-ion batteries, and high theoretical specific energy (Wh/kg) values, especially when light metals are used [1]. Several MAB chemistries were proposed, including alkali, transition, and multivalent metals [2]. Among them, the Li-O<sub>2</sub> cells (LAB) stand out because of the highest theoretical energy density value of 3.5 kWh/kg.

Despite such a promising theoretical performance, many challenging problems still have to be solved to make LAB a consolidated technology. The typical configuration of the LAB cell consists of a lithium metal anode and an air-breathing cathode that is exposed to air or O<sub>2</sub> (Fig. 1a). The two electrodes are separated by a membrane soaked with the electrolyte solution, which is composed of lithium salt dissolved in water or organic solvents [3]. The electrode reactions that take place in an organic LAB are the following:



As it concerns the metal anode, stripping/deposition inherently induces changes in metal surface morphology, dendrite growth, and metal fragmentation into particles with subsequent loss of both electric contact and material. The electrolyte can play a key role by forming a suitable solid electrolyte interface (SEI) that protects the anode and controls the uniform metal deposition. The

membrane is also an important component of LAB and it should be designed properly to avoid or limit the O<sub>2</sub> crossover from the cathode to the anode [4-8]. One of the major challenges for the cycle life of LAB cells is the durability of the Li metal electrode, and several strategies were proposed to increase cell cyclability and safety [9-12].

At the cathode side, during the discharge and recharge processes, the peroxide species are formed and re-oxidized to O<sub>2</sub>. Many strategies were proposed to alleviate cathode passivation with Li<sub>2</sub>O<sub>2</sub> that limits the discharge capacity and causes a recharge overpotential higher than 1 V and recharge voltage even of 4 V, leading to low recharge energy efficiency typically lower than 70% [13]. The use of ionic liquids or superconcentrated electrolytes has been demonstrated a valuable approach. Indeed, these environments are able to stabilise the superoxide anion and promote the so-called solution formation mechanism, which is known to delay cathode clogging with Li<sub>2</sub>O<sub>2</sub> [14-21]. The sluggish kinetics of the oxygen reduction and evolution reactions (ORR/OER) at LAB cathodes can be also promoted by catalysts or redox mediators that are supported on the electrode surface, typically a porous carbon featuring high surface area [22-29]. The optimization of the cathode three-phase-boundary (catalyst–electrolyte–gas) is of paramount importance to achieve high conversion efficiency and fast cell response under high-currents that are limited below 0.5 mA/cm<sup>2</sup>. The current rate response of air breathing LABs is also much affected by the slow natural diffusion of O<sub>2</sub> to the cathode. These passivating products limit the discharge capacity of LABs to values that can be 50% lower than the theoretical ones [30]. Some of these issues can be overcome by exploiting a flow cell design in Lithium-Air Flow Batteries (LAFBs) [31-34]. The main difference to static systems is that LAFBs operate with external tanks that store the O<sub>2</sub>-saturated electrolyte (called catholyte), and with pumps that manage flow circulation (Fig. 1b). The catholyte flow convectively transports O<sub>2</sub> through the porous cathode current collector. This concept was demonstrated by a lab-scale cell assembled with a meso-macroporous template carbon cathode and O<sub>2</sub>-saturated *N*-butyl-*N*-methyl pyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR<sub>14</sub>TFSI): bis (trifluoromethane sulfonyl) imide lithium salt (LiTFSI) 9:1. While electrode porous architecture was effective in promoting ORR at the slowest currents, the O<sub>2</sub> mass transport in IL became crucial at the fastest discharges. A practical discharge capacity of 600 mAh/g of carbon electrode was achieved at 0.2 mA/cm<sup>2</sup>, with a recharge efficiency of 92%. These achievements demonstrated that a flow-cell design enables to: i) overcome the O<sub>2</sub> intrinsic mass transport limitation; ii) pave the way toward a new concept of Li/O<sub>2</sub> cell, where oxygen-harvesting is split from the oxygen reaction process [33], and iii) improve the discharge capacity thanks to the promotion of superoxide diffusion into the electrolyte, the separation and storing of discharge products, and mitigation of current collector

passivation by insulating products [35].

Hybrid LAFBs featuring a Li-ion conducting glass-ceramic (LiSICON type) have also been proposed. The use of the solid electrolytes mitigates oxygen crossover from the cathode to the anode and improves cycle life by protecting the lithium metal surface. This approach was exploited in LAFB that consisted of two different units: The stack composed of lithium metal anode in contact with an organic electrolyte and protected by a solid electrolyte, and a cathodic compartment feed with an O<sub>2</sub>-saturated aqueous catholyte. The second part of the LAFB was a recycling unit that collects/removes the discharge product Li(OH) while simultaneously protecting the LISICON layer from corrosion under strongly alkaline conditions [36, 37].

Additional “recycling” units that exploit redox mediators were also proposed for organic LAFBs. In Ref. [38], the catholyte featured a redox mediator that is reduced at the air electrode and regenerated in the external unit while producing Li<sub>2</sub>O<sub>2</sub>. Therefore, Li<sub>2</sub>O<sub>2</sub> precipitates outside of the cell core. This approach enabled a good cycling performance over 100 cycles.

A LAFB based on redox-mediated ORR and OER reactions was proposed as an effective approach to avoid the surface passivation and pore clogging issues of the air electrode. The reversible formation and decomposition of Li<sub>2</sub>O<sub>2</sub> occurs in an external gas diffusion tank filled with porous material that allows the easy access of redox fluid and O<sub>2</sub> and it is connected to the electrochemical cell stack [39, 40, 41]. This approach enabled to achieve high areal power of 60 and 34 mW/cm<sup>2</sup> when supplied with O<sub>2</sub> and dry air, respectively, and current density of 15 mA/cm<sup>2</sup> [42]. In the development of LAFB, given the high viscosity of the organic catholyte, the fluid dynamics inside the flow frame of the porous cathode strongly affect the cell net power output. By a semi-empirical approach, it was demonstrated that by smart cell geometry it is possible to drastically reduce pressure drops, which are directly proportional to the consumed power. It was demonstrated that the highest net power gain corresponding to a net power of ca. 15 mW within 0–200 rpm pump rate (2.5 mL/s) is achievable by maximizing the flow cross-sectional area through the 3D current collector. Even if the net power output was almost constant over the pump rate range, high pumping regimes provided the highest discharge currents [43].

A breakthrough towards the exploitation of the promised high specific energy of Li/O<sub>2</sub> cell was achieved by the use of a semi-solid catholyte in the so-called Semi-Solid LAFB (SLAFB)(Fig. 1c) [44]. A comparative resume of the main components of the three different lithium-O<sub>2</sub> battery cell concepts, i.e. LAB, LAFB and SLAFB, is presented in Table 1. The operational concept, key component development, and challenging prototyping activities are reported and discussed in the following sections.

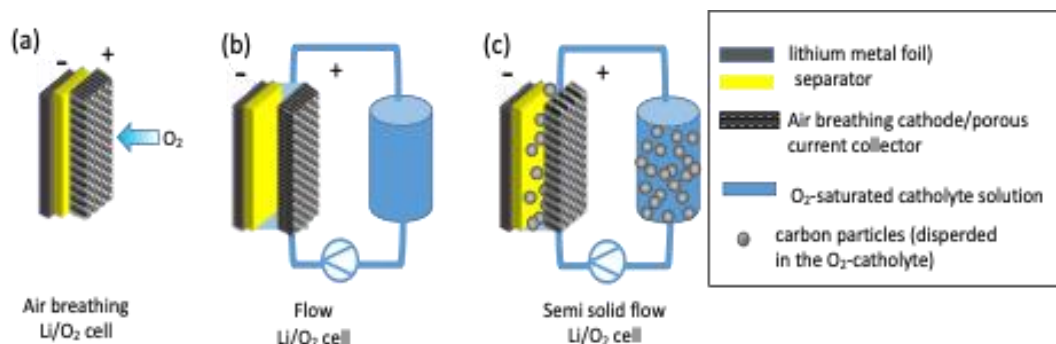


Figure 1. Schemes of a) air-breathing (LAB), b) flow (LAFB), and c) semi-solid flow (SLAFB) Li/O<sub>2</sub> cell.

Table 1. Comparison of components of the lithium-O<sub>2</sub> battery cell concepts, i.e. LAB, LAFB and SLAFB.

Cell type	Acronym	Anode	Cathode	Electrolyte
Air breathing	LAB	Lithium metal	Porous, high surface area, air-breathing carbonaceous cathode	Organic solution with lithium salts, gel, solid-state (ceramic, polymeric) electrolytes
Flow Li/O <sub>2</sub> Cell	LAFB	Lithium metal	Porous current collector, eventually coated with high surface area carbon/catalysts, intercepting the catholyte flow	Organic solution with lithium salts (and eventually mediators), saturated with oxygen (Catholyte)
Semi solid flow Li/O <sub>2</sub> Cell	SLAFB	Lithium metal	Macroporous current collector, eventually coated with high surface area carbon/catalysts, intercepting the semi-solid catholyte flow	Organic solution with lithium salts and carbon particles, eventually modified with mediators or catalysts, saturated with oxygen (semi-solid catholyte)

## 2. Semi-solid flow batteries

Semi-solid redox flow batteries (SRFB) share similar design and same advantages of conventional redox flow batteries (RFB), i.e. energy and power decoupling. Energy sizes with the electrolyte volume, power depends on the reactor dimensions (current collectors, plates). The main difference is that in SRFB the solid electroactive particles are dispersed in the electrolytes [32, 45].

The use of semi-solid catholytes and/or anolytes offers the great advantage of overcoming the solubility limit of active species in the electrolyte, therefore enabling to boost RFB volumetric capacity and energy densities. As an additional key advantage, the use of semi-solid fluids allows designing novel RFBs based on different chemistries that are typically featured by static battery cells with solid electrodes, like Li-ion, Li/S, Li/O<sub>2</sub>, Na-ion, Zn-Ni, Zn-Fe, vanadium RFBs [32, 46-50]. The development of SRFB brings strategic advantages to RFBs: i) the active particles will not crossover through the separator, that can be easily designed approaching the electrolyte bulk conductivity, with advantages in terms of power; ii) electrode active materials that experience volume change during the charge/discharge process, and can be hardly used for long cycle life cells, can be more efficiently used in suspensions; iii) energy demanding and environment

impacting solid electrode manufacturing is avoided, with advantage in terms of costs; iv) cells can be recharged mechanically, i.e. “refilled” by replacing the aged anolyte with a fresh slurry, opening a new concept of “fast” recharge; and v) active materials dispersed in aged slurries can be easily recovered by simple physical separation means (e.g. filtration).

Many challenges are still to be faced in SRFBs. Efficient management of the viscous slurries resulting from the particle suspension is required, along with a smart management of the slurry flow, and improved reactor design. Furthermore, in the case of high-voltage semisolid RFBs, based on the lithium chemistry, the SEI formation represents a critical issue, since it can insulate the active particles and the current collector [51]. Moreover, the slurries should not sediment but feature a stable and efficient electrical percolation network to improve the kinetics of the faradaic processes, and, specifically, the electron transfer between the particles and the current collector [52-56]. The use of viscous semi-solid slurries requires a proper design of the cell architecture. Filter press type cells with macroporous current collectors are typically used for exploration studies and prototyping activities [57, 58]. Moreover, filter press redox flow cell prototypes can be realised through 3D printing, which is a quicker prototypal technological approach than traditional workshop methods, superior in terms of time and costs [60].

### 3. Semi-solid Li/O<sub>2</sub> flow batteries

Semi-Solid Li/O<sub>2</sub> Flow batteries feature a lithium metal anode, a separator, and a semi-solid catholyte (Fig. 1c). The SLAFB catholyte differs from that of other SRFBs’ because the active species, i.e. O<sub>2</sub>, is dissolved in the electrolyte and is continuously fed by an external tank or from the air. Like in LAFB, the catholyte is a carrier that fastens cell feeding. It also controls and regulates cell temperature or pressure, which are important parameters for cell safety and operations. The semi-solid catholyte features dispersed conductive carbon particles that cannot be considered as “active” components but have a unique role in driving the ORR/OER reactions. In the SLAFB, the ORR/OER mainly take place on the dispersed carbon particles, according to the following equations:



The insulating Li<sub>2</sub>O<sub>2</sub> is formed in the suspension crossing the 3D current collector and is readily flown away from the cell core. Consequently, the passivation of the cathode current collector is alleviated and cell discharge capacity dramatically increased. In parallel, the carbon percolating

network multiplies redox sites, the catholyte flow increases  $O_2$  mass transport, and, hence, the current rate response is improved.

The SLAFB concept was demonstrated by a lab-cell prototype that featured a 3D current collector based on reticulated vitreous carbon (RVC) coated with SuperP carbon (SP). The semi-solid catholyte was a suspension of 2% SP in  $O_2$ -saturated solution of tetraethylene glycol dimethyl ether (TEGDME): LiTFSI 9:1. The prototype was capable of operating at high discharge rates (up to  $4 \text{ mA/cm}^2$ ), one order of magnitude higher than the values obtained in conventional air-breathing LAB, with high discharge capacity ( $> 175 \text{ mAh/cm}^2$ ), energy ( $> 500 \text{ mWh/cm}^2$ ) and power ( $> 7 \text{ mW/cm}^2$ ), and low recharge overpotential (3.5 V) (Fig. 2). Notably, the discharge capacity of the SLAFB was limited by the depletion of the lithium metal (Fig. 2a). Indeed, at pump rates below 200 rpm and currents higher than  $3.5 \text{ mA/cm}^2$ , lithium anode gave the main contribution to the cell overvoltage. In these conditions, during the discharge, the lithium potential is raised due to a low diffusion of the  $Li^+$  ions in the bulk electrolyte and/or through the SEI at the lithium surface (Fig. 2d) [58].

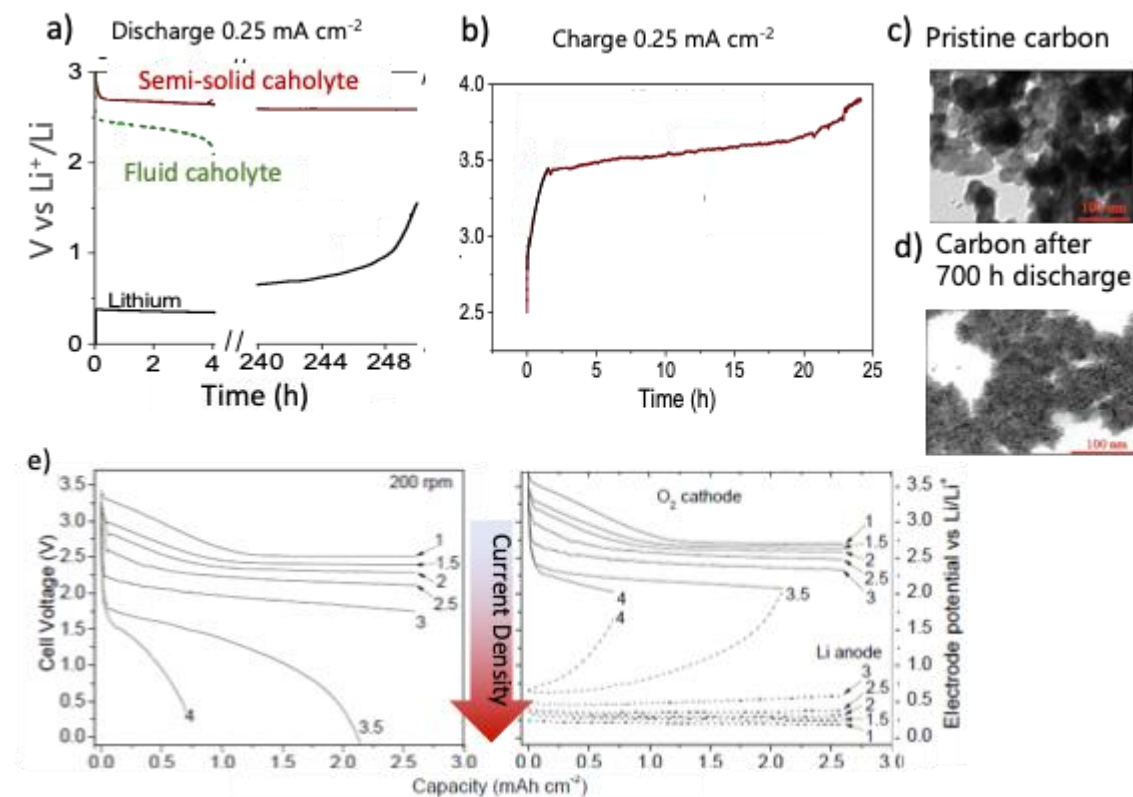


Figure 2. Potential profiles (a) during discharge at  $-0.25 \text{ mA/cm}^2$  of an  $O_2$ -saturated semi-solid catholyte (red) and fluid catholyte (green) and the lithium metal anode or electrolyte; (b) during the charge at  $0.25 \text{ mA/cm}^2$  of a semi-solid catholyte discharged over 45 h; TEM images of the carbon particles (c) before and (d) after discharge, (e)

SLFAB cell voltage and electrode potential profiles under galvanostatic discharges at 200 rpm pump rotation and different current densities (labels indicate the current densities ranging from 1 to 4 mA/cm<sup>2</sup>, cut-off: 2.6 mAh/cm<sup>2</sup> capacity and 2 V vs Li<sup>+</sup>/Li cathode potential). Reprinted from *Electrochimica Acta*, 206, I. Ruggeri, C. Arbizzani, F. Soavi, A novel concept of Semi-solid, Li Redox Flow Air (O<sub>2</sub>) Battery: a breakthrough towards high energy and power batteries, 291-300, Copyright (2016) with permission from Elsevier [44, 58].

Key parameters for the design of high-performance SLAFB are catholyte flow rate, lithium-to-catholyte mass balancing, the carbon content in the semi-solid catholyte, lithium thickness, and current collector size. The higher is the content of the carbonaceous particles dispersed in the semi-solid catholyte that can host the Li<sub>2</sub>O<sub>2</sub> discharge product, the higher are the gravimetric and volumetric performance. It was projected that the main improvements are achievable by increasing the carbon content up to ca. 10%. Above such values, careful control of the rheological properties of the slurry is of paramount importance and only moderate advantages can be obtained. In Ref. [40], it was estimated that 1 kWh/kg<sup>1</sup> and 700 Wh/L could be achieved by using a thick (1200 μm) lithium anode and a slurry with 12% carbon. In turn, the highest projected specific power and power density of 70 W/kg and 20 W/L could be met with a thin (100 μm) lithium anode and 6-8% of carbon [53].

In Refs. [52] and [59] slurries based on different carbon content (SP and pure black, PB) in LiTFSI-TEGDME solutions with salt concentration ranging from 0.5 to 5 mol/kg (solvent-in-salt solution) were investigated to optimize the formulation. Superconcentrated solutions of LiTFSI in TEGDME, for their ionic-liquid-like behavior, are gaining great interest as a new class of stable electrolytes [17, 61]. Compared to SP, the smaller and fractured particles of PB carbon provided pseudoplastic slurries capable of reducing their viscosity at an increased shear rate even at high carbon content (Fig. 2a). The overall effect was the improvement of the electronic percolation, mainly related to the increase of the carbon content, and the electrochemical performance compared to 2% SP-based catholyte. Slurries with a 10% PB were discharged in half-cells at currents as high as 4.5 mA/cm<sup>2</sup> (Fig. 2b) and exhibited promising cycling stability under hundreds of cycles, featuring 4 mAh/cm<sup>2</sup> areal capacity [59]. Notably, the increase of LiTFSI concentration in the liquid phase, and, hence, of the solution ionic strength, contributed to shield carbon interparticle interactions and to achieve a better and more stable carbon dispersion and connection (Fig. 2c). Indeed, slurries with 2% and 4% carbon in 3 and 5 mol/kg LiTFSI-TEGDME featured percolating resistances that were almost 50% and 20% smaller than those of samples with 0.5 mol/kg LiTFSI (Fig. 2d).



The cell core of the lab-scale SLAFB prototype proposed in ref [44] was constituted of a lithium metal anode and porous cathode made of reticulated vitreous carbon (RVC), coated with an SP carbon layer (RVCSP,  $0.385 \text{ cm}^2$ ,  $7 \text{ mg cm}^{-2}$  of SP). The two electrodes were separated by a fibre glass membrane (Fig. 4a and 4b). The semi-solid catholyte was fed through the RVCSP by a peristaltic pump while being continuously enriched with  $\text{O}_{2(g)}$  (Fig. 4c). An additional reference electrode which intercepted the catholyte flow was used to monitor electrode potentials [44].

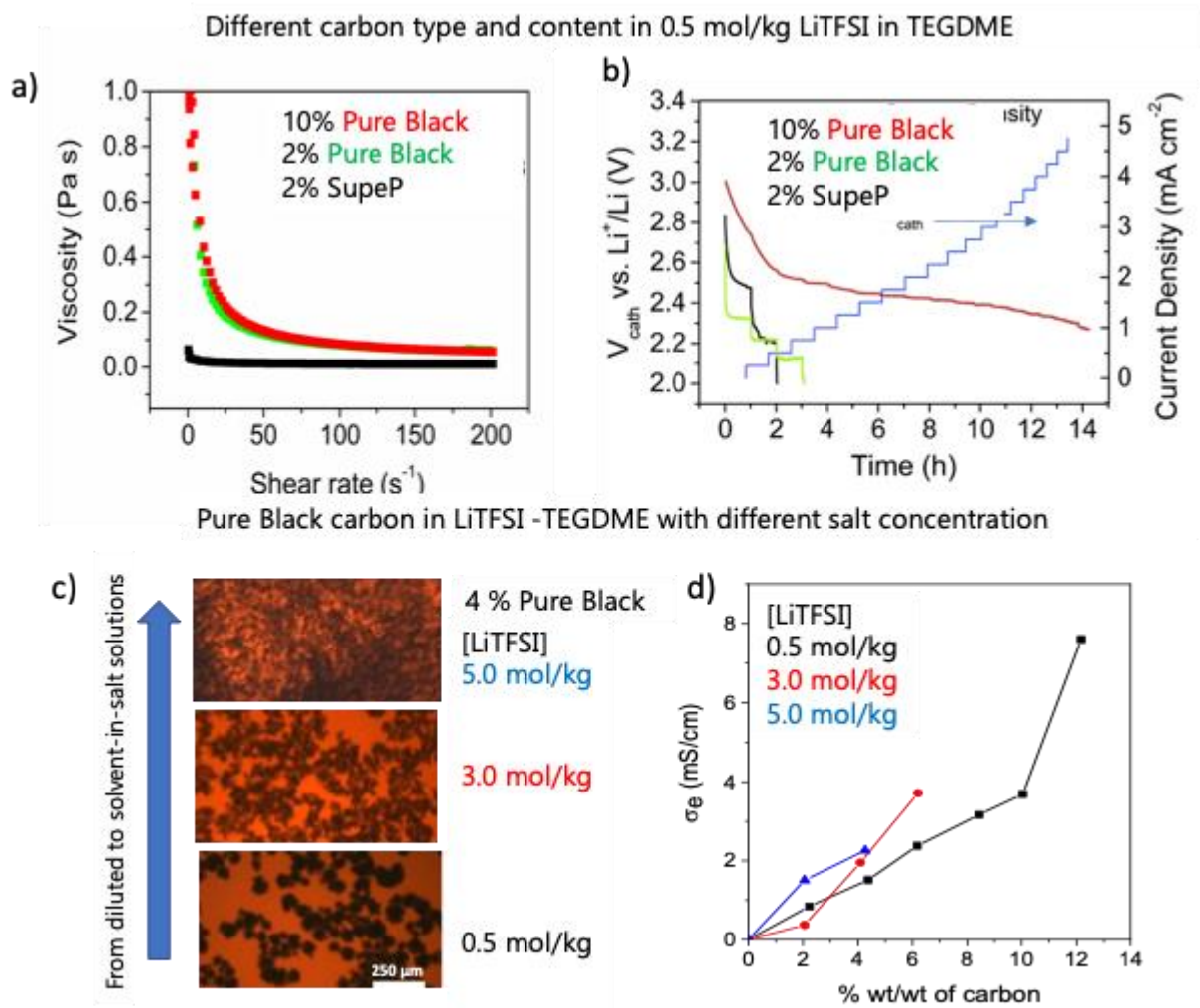


Figure 3. (a) Rheological behavior in terms of viscosity vs shear rate; (b) trends of the potentials of semi-solid catholytes based on PB (10% and 2%) and SP (2%) carbons in 0.5 mol/kg LiTFSI-TEGDME (discharge steps with 1 h and  $2 \text{ mAh/cm}^2$  cut-off); slurries based on PB carbon in LiTFSI-TEGDME with different carbon mass percentages and in different salt concentration (from diluted 0.5 mol/kg to super-concentrated 5 mol/kg) (c) optical fluorescence microscope images with dissolved rhodamine B as dye; (d) electronic conductivity. Reprinted from Carbon, 130, I. Ruggeri, C. Arbizzani, F. Soavi, Carbonaceous catholyte for high energy density semi-solid Li/O<sub>2</sub> flow battery, 749-757, Copyright (2018), with permission from Elsevier [58].

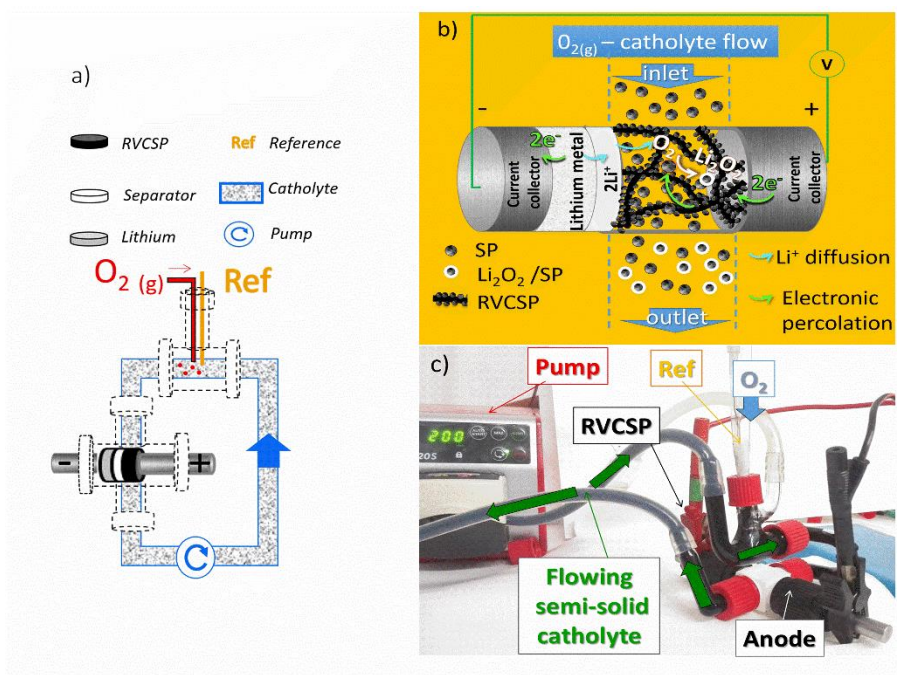


Figure 4. (a, b) Scheme of SLAFB cell and (b) lab-scale prototype under operation. Reprinted from *Electrochimica Acta*, 206, I. Ruggeri, C. Arbizzani, F. Soavi, A novel concept of Semi-solid, Li Redox Flow Air (O<sub>2</sub>) Battery: a breakthrough towards high energy and power batteries, 291-300, Copyright (2016) with permission from Elsevier [40].

For a comparison with other flow battery chemistries, Table 2 compares the practical key performance indexes of SLAFB and Zn- or V- -air flow batteries with that of the most consolidated RFB technology, i.e. the Vanadium redox flow battery (VRFB).

Table 2. Practical, key performance indexes of metal-air flow batteries, compared to VRFB.

Battery chemistry	Open-circuit voltage (OCV)	Specific Capacity	Specific energy	Specific power	Ref.
Semi-solid lithium-air flow battery (SLAFB)	3.2 V	175 mAh cm <sup>-2</sup> (> 250 mAh g <sup>-1</sup> *)	800 Wh kg <sup>-1</sup> *	12 mW cm <sup>-2</sup>	[58] [59]
Flow Li/O <sub>2</sub> Cell (LAFB)	3.2 V	18 – 140 mAh cm <sup>-2</sup>	20-160 Wh kg <sup>-1</sup> **	34 – 60 mW cm <sup>-2</sup>	[42]
Zn-air flow battery (ZAFB)	1.6 V	300 - 870 mAh g <sup>-1</sup>	100 – 600 Wh kg <sup>-1</sup>	100 – 270 mW cm <sup>-2</sup>	[62] [63]
Vanadium- air redox flow battery (VARFB)	1.5 V	15-30 mAh g <sup>-1</sup>	25-40 Wh kg <sup>-1</sup>	20-35 mW cm <sup>-2</sup>	[64]
Vanadium redox flow battery (VRFB)	1.2 V	15-20 mAh L <sup>-1</sup>	25-30 Wh L <sup>-1</sup>	100-120 mW cm <sup>-2</sup>	[32]

\*Including the semi-solid slurry (10% carbon content), the cathode current collector and Li foil

\*\*Including catholyte and Li foil

#### 4. Upscaling semi-solid Li/O<sub>2</sub> flow batteries

The upscale of SLAFB cells requires a holistic R&D approach that includes the optimization of separators, catholyte formulation, lithium metal interface, and cell assembly and management board, while targeting the improvement of nominal power, current rate response, and cyclability. The Spin-off BETTERY Srl designed and developed the first up-scaled SLAFB prototype, i.e. NESSOX (NEw Semi-Solid flow lithium OXYgen battery) (Fig. 5) [www.bettery.eu], under the NESSOX project [https://cordis.europa.eu/project/id/837041/it], and in collaboration with MISTER Smart Innovation [www.laboratoriomister.it]. The prototype featured 12 cm<sup>2</sup> plates that were assembled using a case of Teflon and RVC current collector for the catholyte. The catholyte flow and O<sub>2</sub> feeding were controlled by the control unit that included a peristaltic pump, a flowmeter, and pressure sensors. Figure 5 shows the most representative measurements carried out on the prototype at room temperature performed at 24 mA and 12 mA (Fig. 5). During the discharge, the cell displayed a flat plateau at 2.5 V, while the recharge took place at 3.5 V. It is expected that energy densities as high as 950 Wh/L and 800 Wh/kg (excluding case and control units) can be achieved. These are extremely interesting achievements because they are in line with the results obtained with small lab-scale cells (0.5 cm<sup>2</sup>) and pave the way towards further development and sup-scale of SLAFB.

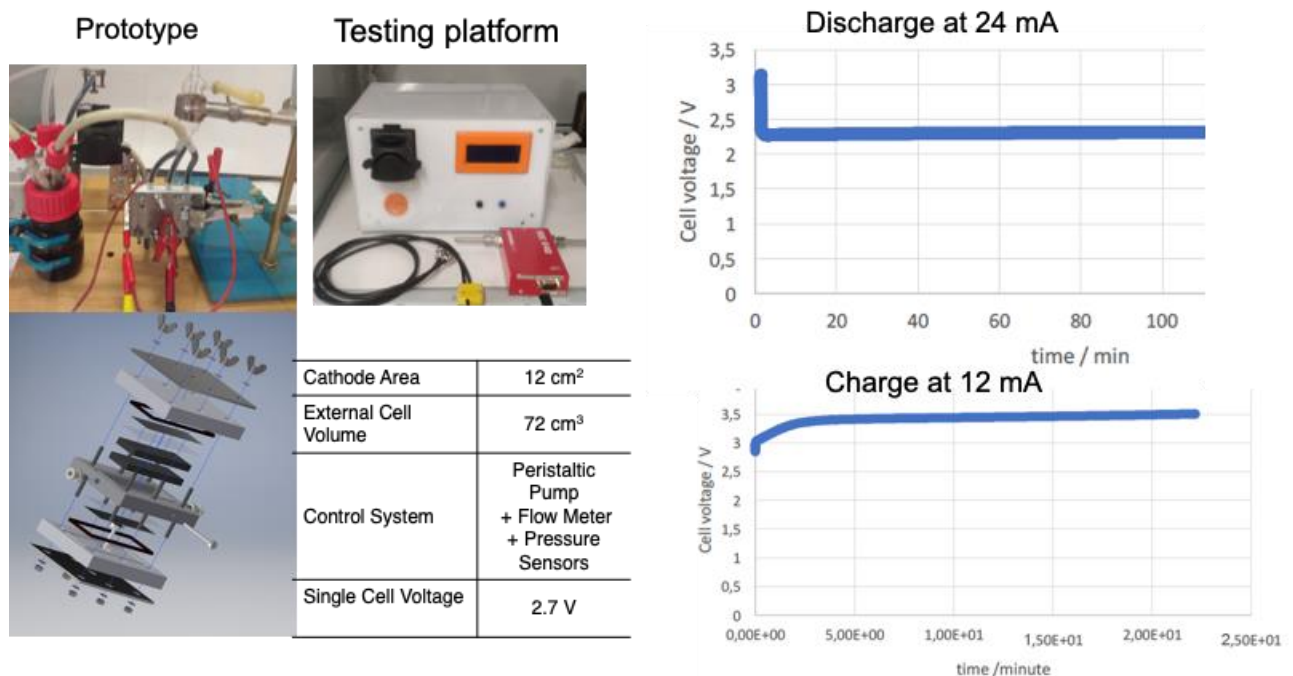


Figure 5. NESSOX prototype and schematic view with the testing platform, and cell discharge and recharge cell voltage profiles [Courtesy of Bettery, internal report https://cordis.europa.eu/project/id/837041/it].

## **5. Conclusions and perspectives**

Herein, we have provided a short review of the recent developments and technological roadmap of Semi-Solid Li/O<sub>2</sub> Flow Batteries (SLAFBs), starting from the static, air-breathing batteries (LAB) to Li/O<sub>2</sub> flow (LAFB) cell configurations, focusing on materials up to cell upscale.

SLAFBs represent a cutting-edge technology that brings in a unique solution the advantages of high specific energy of LAB and the design flexibility of redox flow batteries (RFB). SLAFB can accelerate the market penetration of LABs, by addressing their intrinsic limitations due to limited O<sub>2</sub> mass transport and Li<sub>2</sub>O<sub>2</sub> cathode clogging. However, further steps are still needed both at the fundamental and applied research level for a wide implementation and industry acceptance of this promising technology for energy storage applications.

The paths towards the development of advanced semi-solid catholytes point to new slurries with low viscosity. Improvements are expected by using catalysts or redox mediators dissolved/dispersed in the slurries or supported on porous current collectors, which can further alleviate carbon particle passivation by Li<sub>2</sub>O<sub>2</sub> and accelerate OER and ORR kinetics. However, one of the biggest challenges is the optimization of the lithium metal interface. Indeed, the semi-solid catholyte enables cell operation at current areal densities that are above the typical regimes of static lithium-metal batteries. In addition, oxygen crossover through the separator is detrimental not only for the cell self-discharge but also because it negatively affects the stability and electrochemical performance of the lithium metal interface. The substitution of lithium metal with competitive semi-solid anolytes, like those based on lithium-ion insertion active materials or alloys, can be a valuable option to circumvent lithium metal limitations.

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## References

- [1] A. G. Olabi, E. T. Sayed, T. Wilberforce, A. Jamal, A. H. Alami, K. Elsaid, S. M. A. Rahman, S. K. Shah, M. A. Abdelkareem, Metal-air batteries—A review, *Energies* 14 (2021) 7373-741.
- [2] X. Zhang, X.-G. Wang, Z. Xie, Z. Zhou, Recent progress in rechargeable alkali metal-air batteries, *Green Energy Environ.* 1 (2016) 4-17.
- [3] T. Liu, J. P. Vivek, E. W. Zhao, J. Lei, N. Garcia-Araez, C. P. Grey, Current challenges and routes forward for nonaqueous lithium–air batteries, *Chem. Rev.* 120 (2020) 6558–662.
- [4] R. S. Assary, J. Lu, P. Du, X. Luo, X. Zhang, Y. Ren, L. A. Curtiss and K. Amine, The effect of oxygen crossover on the anode of a Li–O<sub>2</sub> battery using an ether-based solvent: Insights from experimental and computational studies, *ChemSusChem* 6 (2013) 51-55.
- [5] X. Zou, Q. Lu, K. Liao, Z. Shao, Towards practically accessible aprotic Li-air batteries: Progress and challenges related to oxygen-permeable membranes and cathodes, *Energy Storage Mater.* 45 (2022) 869-902.
- [6] J. Li, L. Hou, M. Yu, Q. Li, T. Zhang, H. Sun, Review and recent advances of oxygen transfer in Li-air batteries, *ChemElectroChem* 8 (2021) 3588–3603.
- [7] E. Wang, E. W. Zhao, C. P. Grey, New magnetic resonance and computational methods to study crossover reactions in Li-air and redox flow batteries using TEMPO, *J. Phys. Chem. C* 125 (2021) 27520–27533.
- [8] X. Zou, K. Liao, D. Wang, Q. Lu, C. Zhou, P. He, R. Ran, W. Zhou, W. Jin, Z. Shao, Water-proof, electrolyte-nonvolatile, and flexible Li-Air batteries via O<sub>2</sub>-permeable silica-aerogel-reinforced polydimethylsiloxane external membranes, *Energy Storage Mater.* 27 (2020) 297–306.
- [9] Wei Liang, F. Lian, N. Meng, J. Lu, L. Ma, C.-Z. Zhao, Q. Zhang, Adaptive formed dual-phase interface for highly durable lithium metal anode in lithium–air batteries, *Energy Storage Mater.* 28 (2020) 350-356.
- [10] H. Irfan, A. M. Shanmugharaj, Organosilane based artificial solid electrolyte interface layer for stable metallic lithium anode, *Appl. Surf. Sci.* 586 (2022) 152806-152815.
- [11] Z. Wang, Y. Cao, J. Zhou, J. Liu, X. Shen, H. Ji, C. Yan, Tao Qian, Processing robust lithium metal anode for high-security batteries: A minireview, *Energy Storage Mater.* 47 (2022) 122–133.
- [12] W.-L. Bai, Z. Zhang, X. Chen, X. Wei, Q. Zhang, Z.-X. Xu, Y.-S. Liu, B. Chang, K.-X. Wang, J.-S. Chen, Boosting the electrochemical performance of Li–O<sub>2</sub> batteries with DPPH redox mediator and graphene-luteolin-protected lithium anode, *Energy Storage Mater* 31 (2020) 373–381.

- [13] W.-J. Kwak, Rosy, D. Sharon, C. Xia, H. Kim, L. R. Johnson, P. G. Bruce, L. F. Nazar, Y.-K. Sun, A. A. Frimer, M. Noked, S. A. Freunberger, D. Aurbach, Lithium–oxygen batteries and related systems: Potential, status, and future, *Chem. Rev.* 12 (2020) 6626–6683.
- [14] I. Ruggeri, C. Arbizzani, S. Rapino, F. Soavi, Oxygen Redox Reaction in Ionic Liquid and Ionic Liquid-like Based Electrolytes: A Scanning Electrochemical Microscopy Study, *J. Phys. Chem. Lett.* 10 (2019) 3333-3338.
- [15] S. Monaco, A. M. Arangio, F. Soavi, M. Mastragostino, E. Paillard, S. Passerini, An electrochemical study of oxygen reduction in pyrrolidinium-based ionic liquids for lithium/oxygen batteries, *Electrochim. Acta* 83 (2012) 94-104.
- [16] F. Soavi, S. Monaco, M. Mastragostino, Catalyst-free porous carbon cathode and ionic liquid for high efficiency, rechargeable Li/O<sub>2</sub> battery, *J. Power Sources* 224 (2013) 115-119.
- [17] F. Messaggi, I. Ruggeri, D. Genovese, N. Zaccheroni, C. Arbizzani, F. Soavi, Oxygen redox reaction in lithium-based Electrolytes: from salt-in-solvent to solvent-in-salt, *Electrochim. Acta* 245 (2017) 296-302.
- [18] A. C. Luntz, B. D. McCloskey, Li–air batteries: Importance of singlet oxygen, *Nat. Energy* 2 (2017) 1-2.
- [19] K. Nishioka, M. Tanaka, H. Fujimoto, T. Amaya, S. Ogoshi, M. Tobisu, S. Nakanishi, Overlooked factors required for electrolyte solvents in Li–O<sub>2</sub> battery: Capabilities of quenching <sup>1</sup>O<sub>2</sub> and forming highly-decomposable Li<sub>2</sub>O<sub>2</sub>, *Angew. Chem. Int. Ed.* e202112769 (2022) 1-9.
- [20] B. Liu, W. Xu, P. Yan, S. T. Kim, M. H. Engelhard, X. Sun, D. Mei, J. Cho, C.-M. Wang, J.-G. Zhang, Stabilization of Li metal anode in DMSO-based electrolytes via optimization of salt–solvent coordination for Li–O<sub>2</sub> batteries, *Adv. Energy Mater.* (2017) 1602605- 1602614.
- [21] Q. Dong, Xi. Yao, Y. Zhao, M. Qi, X. Zhang, H. Sun, Y. He, D. Wang, Cathodically stable Li-O<sub>2</sub> battery operations using water-in-salt electrolyte, *Chem* 4 (2018) 1345–135.
- [22] L. Ren, L. Wang, D. Du, R. Zheng, Y. Yan, M. He, Z. Ran, M. Li, C. Shu, Rationalizing the effect of surface electronic structure on oxygen electrocatalyst for high performance lithium-oxygen battery, *Electrochim. Acta* 407 (2022) 139891-139899.
- [23] S. Li, H. Guo, S. He, H. Yang, K. Liu, G. Duan, S. Jiang, Advanced electrospun nanofibers as bifunctional electrocatalysts for flexible metal-air (O<sub>2</sub>) batteries: Opportunities and challenges, *Mater. Des.* 214 (2022) 110406-110419.
- [24] D. Li, J. Liang, S. J. Robertson, Y. Chen, N. Wang, M. Shao, Z. Shi, Heterogeneous Bimetallic Organic Coordination Polymer-Derived Co/Fe@NC Bifunctional Catalysts for Rechargeable Li–O<sub>2</sub> Batteries, *ACS Appl. Mater. Interfaces* 14 (2022) 5459–5467.

- [25] J. Shen, H. Wu, W. Sun, Q. Wu, S. Zhen, Z. Wang, K. Sun, Biomass-derived hierarchically porous carbon skeletons with in situ decorated IrCo nanoparticles as high-performance cathode catalysts for Li–O<sub>2</sub> batteries, *J. Mater. Chem. A* 7 (2019) 10662–10671.
- [26] A. Tkacheva, J. Zhang, B. Sun, D. Zhou, G. Wang, A. M. McDonagh, TEMPO-ionic liquids as redox mediators and solvents for Li–O<sub>2</sub> batteries, *J. Phys. Chem. C* 124 (2020) 5087–5092
- [27] Z. Liang, Q. Zou, J. Xie, Y. Chun, Suppressing singlet oxygen generation in lithium–oxygen batteries with redox mediators, *Energy Environ. Sci.* 13 (2020) 2870–2877.
- [28] H. Zhong, J. Wang, Y. Wang, P. He, H. Zhou, Progress and prospects in redox mediators for highly reversible lithium–oxygen batteries: A minireview, *Energy Fuels* 35 (2021) 19302–19319
- [29] Y. Ko, H. Park, B. Kim, J. S. Kim, K. Kang, Redox Mediators: A Solution for Advanced Lithium–Oxygen Batteries, *Trends Chem.* 1 (2019) 349–360.
- [30] K. Hayat, L. F. Vega, A. AlHajaj, What have we learned by multiscale models on improving the cathode storage capacity of Li-air batteries? Recent advances and remaining challenges, *Renew. Sust. Energ. Rev.* 154 (2022) 111849–111865.
- [31] X. Han, X. Li, J. White, C. Zhong, Y. Deng, W. Hu, T. Ma, Metal–air batteries: From static to flow system, *Adv. Energy Mater.* 8 (2018) 1801396–1801424.
- \*[32] E. Sánchez-Díez, E. Ventosa, M. Guarnieri, A. Trovò, C. Flox, R. Marcilla, F. Soavi, P. Mazur, E. Aranzabe, R. Ferret, Redox flow batteries: Status and perspective towards sustainable stationary energy storage, *J. Power Sources* 481 (2021) 228804–228826.
- Review article on redox flow batteries. This article aims at providing a critical review of the redox flow batteries technologies that could potentially fulfil the requirements for large-scale storage.
- \*[33] S. Monaco, F. Soavi, M. Mastragostino, Role of oxygen mass transport in rechargeable Li/O<sub>2</sub> batteries operating with ionic liquids, *J. Phys. Chem. Lett.* 4 (2013) 1379–1382.
- A novel configuration of flow lithium oxygen battery exploiting an ionic liquid electrolyte is reported. This novel combination allows the authors to demonstrate that the response of the oxygen electrodes in the IL electrolyte is limited by the oxygen mass transport.
- [34] Y. G. Zhu, F. W. T. Goh, Q. Wang, Redox catalysts for aprotic Li–O<sub>2</sub> batteries: Toward a redox flow system, *Nano Mater. Sci.* 1 (2019) 173–183.
- [35] B. Kim, K. Takechi, S. Ma, S. Verma, S. Fu, A. Desai, A. S. Pawate, F. Mizuno, P. J. A. Kenis, Non-aqueous primary Li–Air flow battery and optimization of its cathode through experiment and modelling, *ChemSusChem* 10 (2017) 4198–4206.
- [36] W. Yu, W. Shang, P. Tan, B. Chen, Z. Wu, H. Xu, Z. Shao, M. Liu, M. Ni, Toward a new generation of low cost, efficient, and durable metal–air flow batteries, *J. Mater. Chem. A* 7 (2019) 26744–26768.

[37] X. J. Chen, A. Shellikeri, Q. Wu, J. P. Zheng, M. Hendrickson, E. J. Plichta, A high-rate rechargeable Li-air flow battery, *J. Electrochem. Soc.* 160 (2013) A1619-A1623.

\*\*[38] P. He, Y. Wang, H. Zhou, A Li-air fuel cell with recycle aqueous electrolyte for improved stability, *Electrochem. Commun.* 12 (2010) 1686-1689.

This article reports about a new design of a lithium-air fuel cell that improves the cell stability. The fuel cell features an aqueous electrolyte with a LISICON membrane to protect the metallic lithium anode.

\*\*[39] Y. G. Zhu, C. Jia, J. Yang, F. Pan, Q. Huang, Q. Wang, Dual redox catalysts for oxygen reduction and evolution reactions: towards a redox flow Li–O<sub>2</sub> battery, *Chem. Commun.* 51 (2015) 9451-9454.

In this study, a redox flow lithium–oxygen battery by using soluble redox catalysts was demonstrated for large-scale energy storage. The new battery configuration enables the reversible formation and decomposition of Li<sub>2</sub>O<sub>2</sub> via redox targeting reactions in a gas diffusion tank.

[40] Y. G. Zhu, X. Wang, C. Jia, J. Yang, Q. Wang, Redox-mediated ORR and OER reactions: Redox flow lithium oxygen batteries enabled with a pair of soluble redox catalysts, *ACS Catal.* 6 (2016) 6191–6197.

[41] Y. G. Zhu, Q. Liu, Y. Rong, H. Chen, J. Yang, C. Jia, L. J. Yu, A. Karton, Y. Ren, X. Xu, S. Adams, Q. Wang, Proton enhanced dynamic battery chemistry for aprotic lithium–oxygen batteries, *Nat. Commun.* 8 (2017) 14308-14315.

\*\*[42] Y. G. Zhu, F. W. T. Goh, R. Yan, S. Wu, S. Adams, Q. Wang, Synergistic oxygen reduction of dual redox catalysts boosting the power of lithium–air battery, *Phys. Chem. Chem. Phys.* 20 (2018) 27930-27936.

In this study, a redox flow lithium–oxygen battery based on gas diffusion tank configuration enables high power output and the use of dry air.

\*\*[43] F. Poli, L. K. Ghadikolaei, F. Soavi, Semi-empirical modeling of the power balance of flow lithium/oxygen batteries, *Appl. Energy* 248 (2019) 383-389.

In this study, the authors investigate how different design of the flow frame of organic lithium oxygen flow batteries impact the net power balance of the system.

\*\*[44] I. Ruggeri, C. Arbizzani, F. Soavi, A novel concept of semi-solid, Li redox flow air (O<sub>2</sub>) battery: a breakthrough towards high energy and power batteries, *Electrochim. Acta* 206 (2016) 291-300.

In this study, a radically new battery concept is demonstrated, i.e. non-aqueous Li/O<sub>2</sub> battery operating with a semisolid, flowable catholyte. The proof-of-concept is proven by a catholyte



based on 2 wt% Super P carbon dispersed in tetraethylene glycol dimethyl ether – lithium bis(trifluoromethane)sulfonimide.

[45] K. Chayambuka, J. Fransaer, X. Dominguez-Benetton, Modeling and design of semi-solid flow batteries, *J. Power Sources* 434 (2019) 226740- 226750.

[46] L. Zhang, X. Wu, W. Qian, H. Zhang, S. Zhang, Lithium slurry flow cell, a promising device for the future energy storage, *Green Energy Environ.* 6 (2021) 5-8.

[47] K.-S. Oh, J.-H. Kim, S.-H. Kim, D. Oh, S.-P. Han, K. Jung, Z. Wang, L. Shi, Y. Su, T. Yim, S. Yuan, S.-Y. Lee, Single-ion conducting soft electrolytes for semi-solid lithium metal batteries enabling cell fabrication and operation under ambient conditions, *Adv. Energy Mater.* 11 (2021) 2101813-2101823.

[48] S. Li, H. Wang, J. Cuthbert, T. Liu, J. F. Whitacre, K. Matyjaszewski, A semiliquid lithium metal anode, *Joule* 3 (2019) 1637–1646.

[49] C. Zhang, L. Guo, C. Deng, H. Huang, Y. Cheng, Semi-solid reactive interfaces based on ZnO@C core-shell materials for zinc-iron flow batteries, *Chem. Eng. Sci.* 250 (2022) 117402-117409.

[50] Y. G. Zhu, T. Malai Narayanan, M. Tulodziecki, H. Sanchez-Casalongue, Q. C. Horn, L. Meda, Y. Yu, J. Sun, T. Regier, G. H. McKinley, Y. Shao-Horn, High-energy and high-power Zn–Ni flow batteries with semi-solid electrodes, *Sustain. Energy Fuels* 4 (2020) 4076–4085.

[51] E. Ventosa, G. Zampardi, C. Flox, F. La Mantia, W. Schuhmann, J. R. Morante, Solid electrolyte interphase in semi-solid flow batteries: a wolf in sheep's clothing, *Chem. Commun.* 51.81 (2015) 14973-4976.

\*\*[52] A. Brilloni, F. Poli, G. E. Spina, D. Genovese, G. Pagnotta, F. Soavi, Improving the electrical percolating network of carbonaceous slurries by superconcentrated electrolytes: An electrochemical impedance spectroscopy study, *ACS Appl. Mater. Interfaces* 13 (2021) 13872-13882.

In this study, the authors investigate how the concentration of LiTFSI salt in TEGDME solution affects the percolation threshold of carbonaceous suspension.

[53] F.-J. Zhang, H.-T. Zhang, Applications of nanocarbons in redox flow batteries, *New Carbon Mater.* 36 (2021) 82-92.

[54] M. Mourshed, S. M. Rezaei Niya, R. Ojha, G. Rosengarten, J. Andrews, B. Shabani, Carbon-based slurry electrodes for energy storage and power supply systems, *Energy Storage Mater.* 40 (2021) 461–489.

[55] J. Lohaus, D. Rall, M. Kruse, V. Steinberger, M. Wessling, On charge percolation in slurry electrodes used in vanadium redox flow batteries, *Electrochem. Commun.* 101 (2019) 104–108.

[56] K. Percin, A. Rommerskirchen, R. Sengpiel, Y. Gendel, M. Wessling, 3D-printed conductive static mixers enable all-vanadium redox flow battery using slurry electrodes, *J. Power Sources* 379 (2018) 228–233.

[57] S. Hamelet, D. Larcher, L. Dupont, J.-M. Tarascon, Silicon-based non aqueous anolyte for Li redox-flow batteries, *J. Electrochem. Soc.* 160 (2013) 516–520.

[58] F. Soavi, I. Ruggeri, C. Arbizzani, Design study of a novel, semi-solid Li/O<sub>2</sub> redox flow battery, *ECS Trans.* 72 (2016) 1-9.

\*\*[59] I. Ruggeri, C. Arbizzani, F. Soavi, Carbonaceous catholyte for high energy density semi-solid Li/O<sub>2</sub> flow battery, *Carbon* 130 (2018) 749-757.

The electrochemical response of different formulations of carbonaceous catholyte based on LiTFSI solution in TEGDME for semi-solid lithium oxygen batteries is investigated.

[60] F. Arenas, F.C. Walsh, C. Ponce de Léon. 3D-printing of redox flow batteries for energy storage: A rapid prototype laboratory cell, *ECS J. Solid State Sci.* 4 (2015) 3080–P3085.

[61] T. Tamura, T. Hachida, K. Yoshida, N. Tachikawa, K. Dokko, M. Watanabe, New glyme–cyclic imide lithium salt complexes as thermally stable electrolytes for lithium batteries, *J. Power Sources* 195 (2010) 6095-6100.

[62] A. Abbasi, S. Hosseini, A. Somwangthanaroj, R. Cheacharoen, S. Olaru, S. Kheawhom, Discharge profile of a zinc-air flow battery at various electrolyte flow rates and discharge currents, *Sci. Data* 7 (2020) 196-203.

[63] M. Bockelmann, K. Ulrich, T. Turek, Electrically rechargeable zinc-oxygen flow battery with high power density, *Electrochem. Commun.* 69 (2016) 24-27.

[64] X. Han, X. Li, J. White, C. Zhong, Y. Deng, W. Hu, T. Ma, Metal-air batteries: From static to flow system. *Adv. Energy Mater.* (2018) 1801396-1801423.