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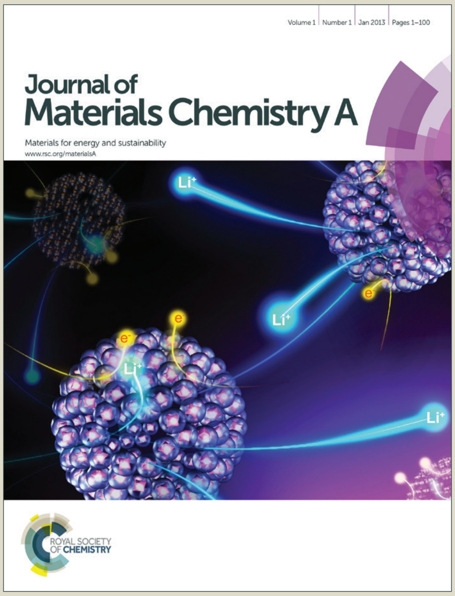

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Use of ion-selective polymer membranes for an aqueous electrolyte rechargeable Li-ion/polysulphide battery

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Abstract

Aqueous electrolyte Li-ion/polysulphide batteries offer great promise due to the use of low-cost and abundant raw materials. Following up our previous studies in which we explored a totally new practical battery chemistry coupling a well-known cathode material in Li-ion batteries (i.e. $LiMn_2O_4$) with a dissolved polysulphide anode, herein we aim to further develop the system by replacing ceramic membrane with an ion-selective polymer membrane allowing much cost-effective and higher energy density options. After tuning the osmotic movements inside the membrane, dissolved polysulphide leakage from one compartment to another is successfully eliminated. With additional use of porous silica serving as an absorbent for sulphur-based gaseous products, a 1.5 V average voltage together with a stable cycling profile over 200 cycles at high current density regimes are easily achieved.

Key Words: Ion selective membranes, aqueous electrolyte, polysulphide, $LiMn_2O_4$, Li-S batteries, energy storage, H_2S adsorption, porous silica

1. Introduction

Storage is one of the essential components of the forthcoming energy supply system to make use of renewable energy sources with fluctuating power output. Load-levelling systems to meet peak-power demands are highly important for grid operation. So the challenge is to develop new storage means. Aside from hydroelectric storage, numerous storage technologies enlisting supercapacitors, electrochemical batteries, fly wheels, compressed air, do exist and cover a broad spectrum of the power output–energy storage domain[1]. The rechargeable batteries are highly preferable among the various energy storage technologies due to their large-scale storage abilities, high energy conversion efficiencies and simple maintenance[2]. To date, particularly, Li-ion batteries have been powering the portable electronics as well as electrical vehicles (EVs). In contrast, they still fall short for grids applications because of both, their high costs and inherent safety issues related to the use of flammable organic electrolytes. Thus, the development of alternative low cost battery technologies is becoming essential. Aware of such a cost issue scientists are exploring new strategies by focussing mainly on the electrolyte which is the most costly component of today's Li-ion systems. An obvious solution could be to switch back to aqueous electrolytes.

Although the use of aqueous electrolytes in the field of Li-ion batteries dates back to 1994[3], the progress on improving their performances were limited. One of the main reasons for these limitations is nested in the low thermodynamic stability of water, 1.23 V, which is too narrow to achieve high operational voltages. Luckily, slow kinetic secondary reactions can occasionally play in our favour as it does for the lead-acid batteries which function at near $\approx$ 2.1 V, but this is still non-sufficient to compete with non-aqueous electrolytes.

To preserve high voltage utilisation, strategies aiming towards the development of two compartment cell configurations to enable the use of different electrolytes at the positive and negative electrode are presently explored. Along that line, an acidic–alkaline double electrolyte primary battery operating at a voltage approaching to 3.0 V has already been reported[4]. Moreover, water soluble redox couples as cathode (or so called catholyte) together with a metallic lithium functioning in a non-aqueous electrolyte as anode were suggested as new concept of alkali-ion batteries[5]. Along that concept Li-iodine batteries using triiodide/iodide couple[6] or Li-bromide batteries using Br_2/Br^- couples[7] have already been reported. However, all these approaches require utilizing a high cost and fragile lithium ion conducting glass ceramic membrane, denoted LIC-GC, made of a combination of Li_2O–Al_2O_3–SiO_2–P_2O_5–TiO_2–GeO_2, to separate between aqueous and non-aqueous electrolytes.

Although elegant for conceptual demonstration, such a heavy and brittle ionic conducting ceramic is still questionable for practical applications.

Turning to the Li-S technology, it is worthwhile mentioning that the use of aqueous electrolyte was suggested more than two decades ago by Licht and co-workers[8] and put in practice few years later for polysulphides-based batteries as well as solar cells[9-12]. In 2013, Visco *et al.* have developed a high performance rechargeable Li-S battery using Li_2S in an aqueous cathode[13]. A still remaining down side, cost-wise, of their approach is rooted in the use of a two compartment cell having a ceramic conducting membrane to separate the aqueous and non-aqueous electrolyte.

Recently, our group demonstrated for the first time an aqueous electrolyte Li/ion-polysulphide battery coupling a well-known cathode material ($LiMn_2O_4$) with dissolved polysulphides as anode (so called anolyte). The cell shows an output voltage of ~1.5 V with sustained capacities of ~110 mAh g^{-1} at C/2 rate for more than 100 cycles, resulting almost 80Wh/kg energy densities which could compete with those of NiMH or Pd-acid aqueous electrolyte rechargeable batteries[14]. Additionally the solubility of active sulphur can reach up to 12 M[13] allowing much higher energy densities. However, the cell was still using a glass ceramic membrane[14]. Searching further for cost reduction, an obvious implementation was to replace the ceramic membrane. Herein, we report a Li-ion/polysulphide battery using an ion-selective polymer membrane namely a perfluorosulfonate ionomer (Nafion) rather than a ceramic membrane as separator[15]. In the field of batteries, Nafion has already been used as i) a proton conducting membrane for fuel cells[15], ii) a binder for alloy negative electrodes in Li-ion batteries[16], iii) covering substance for carbon-sulphur composite electrode in order to trap dissolved polysulphides within the composite[17] and iv) to obtain a functional separator either for Li-S[18] or room temperature Na-S[19] batteries because of its effectiveness in reducing polysulphide dissolution. Therefore, to the best of our knowledge Nafion was never used in the field of aqueous electrolytes lithium batteries. Whatever, using such a modification we could assembled a less costly Li/ion-polysulphide showing better performances than ceramic-based cells in terms of cycle life and rate capability.

2. Experimental

Materials and Electrode Preparations:

$LiMn_2O_4$, polyvynidilene fluoride (PVDF) and n-methyl pyrrolidone (NMP) were used as received from Sigma Aldrich. Working electrode (WE) for CV measurement were prepared by mixing $LiMn_2O_4$ powders with Ketjen-black carbon and an organic binder (PVDF), in a weight ratio of 80:10:10 in NMP. After stirring, the mixture was casted on a stainless steel electrode and then dried at 100 ^oC for 5 h.

The aqueous polysulphide solutions were made by mixing various amounts potassium (poly)sulphide (>42 % K_2S) powders (Sigma-Aldrich) into a 0.5 M Li_2SO_4 aqueous electrolyte.

A swagelok-type hardware was used to assemble the cells. The positive electrode was made from a $LiMn_2O_4$ containing slurry (as described above) which was casted on a stainless steel disk electrode and dried at 100 ^oC for 5 h. The electrode area was 0.9 cm^2, and the weight of active material was typically in the range of 2–3 mg for each sample. A 0.15 ml aqueous polysulphide solution together with 5mg Ketjen black carbon powder as conductive additive was used as the counter electrode (CE). Last, a 25.4 µm thick NAFION® Membrane NR-211, supplied from Ion Power Inc., was used as the separator.

Electrochemistry:

All potentials are reported, if not specified otherwise, versus the standard calomel electrode (SCE). The electrochemical characterization was realized using a VMP-3 instrument from Biologic performed in both cyclic voltammetry (CV) and galvanostatic cycling modes with potential limitation (GCPL). CV measurements were performed with a 3-electrode cell configuration using a 2.5 M or 0.5 M Li_2SO_4 aqueous electrolyte. A scan rate of 0.2 mV/s over 0.4-1.2 V vs SCE was applied for $LiMn_2O_4$. For the dissolved polysulphide the CV test was done at a scan rate of 5 mV/s over -1.0 to 0.3 V (vs SCE). In both cases, carbon coated stainless steel was used as CE and SCE as reference electrode.

For the full cell configuration, experiments were carried out using two-electrode Swagelok-type cells. The electrolyte consisted of a solution of 0.5 M or 2.5 M of Li_2SO_4 in water. The cells were tested in the 0.2 to 1.6 V voltage range with a current density of 2 C or 10 C. In general, the cells were assembled with an excess of polysulphide to compensate for the eventual elimination of gaseous active material. Based on the theoretical capacity value of $LiMn_2O_4$ and dissolved polysulphide, the anolyte to cathode weight ratio was usually taken as 2.5. Lastly, and solely when specified, 5mg SBA-15, synthesized according to the method described in reference[20], was mixed with 5 mg Ketjen black carbon and placed at the polysulphide side.

Characterizations:

Cycling experiments coupled with mass spectrometer measurements were carried out galvanostatically at room temperature with a cycling current density of 2C. The gases were measured via Mass spectrometer (Netzsch QMS 403 Aeolos) operating under primary vacuum. Gaseous product signals were recorded prior cycling the cell and after 30 cycles.

The BET surface area and pore volume of the SBA-15 was evaluated by nitrogen sorption at 77K using a Micromeritics ASAP2020 apparatus. The sample was degassed at 150°C for 6h prior to measurement.

Microstructural analyses were done using a transmission electron microscope (TEM-FEI TECNAI F20 S-TWIN) fitted with a scanning mode and both high-angle annular dark-field (HAADF) detector and EDAX EDS.

3. Results and Discussions

Prior assembling a full cell configuration, membrane leakage and polysulphide diffusion tests were performed. To do so, a known amount of polysulphide (~1.5 M) was dissolved in an aqueous electrolyte and placed in a glass vial covered with a Nafion membrane. Then the well tighten polysulphide containing vials were dipped into aqueous electrolytes whose salt concentrations vary as shown in Fig. 1. We initially checked the effect of having different salt concentrations in each side of the Nafion membrane by first dissolving 1.5 M polysulfide into a 2.5 M Li_2SO_4 aqueous electrolyte (Fig. 1a) and into a 0.5M Li_2SO_4 aqueous electrolyte (Fig.1b), both being dipped into a 0.5 M Li_2SO_4 aqueous electrolyte. As expected, due to the repulsive interaction between the negatively charged membranes (SO_3^- groups) and negatively charged polysulphides, we did not observe any leakage of the polysulphides for at least one day. Nevertheless, during that waiting time there is an increase of the water level in the polysulfide containing compartment due to water displacement. This contrast with the samples left for 3 days for which there is a clear appearance of yellowish colour, indicative of the diffusion of polysulphide through the Nafion membrane. Such diffusion being faster for the larger salt concentration gradient between the two compartments (Fig. 1a). Similar tests were repeated when the salt concentration between both compartments was kept close to equilibrium (Fig. 1c) and in this case we could not see any polysulphide diffusion through the membrane even after 5 months of rest. Shortly, these simple experiments remind us the osmotic pressure phenomenon and rise our awareness about carefully tuning the concentration gradient across the membrane when assembling the full cell to prevent polysulphide diffusion with the lowest concentration gradient being the most suitable solution.

We next implemented the aforementioned conditions for assembling two cells having salts concentrations through the Nafion membrane in equilibrium (conditions of Fig. 1c) and in non-equilibrium (conditions of Fig. 1b). Both cells (Fig. 2a) shows similar capacity for the first cycle, but rapidly differ with a sharp capacity decay for the cell having a non-equilibrated salt concentration (red dots) prior to stabilized after 10 cycles as opposed to a smooth capacity increase for the cell having an equilibrated concentration (black dots). The capacity fading is much drastic (bearing in mind that a complete cycle takes less than one hour) compared to the leakage test which did not reveal any diffusion of polysulfide species through the membrane for at least one day (Fig. 1). One possible reason is nested in the presence of an electrical field through the membrane which could enhance the migration of polysulphides towards the $LiMn_2O_4$ side, hence decreasing the concentration difference between both sides and explaining why the capacity stabilizes after 10 cycles. The better cycling performances (black dots) measured for the cell with equilibrium concentration is reminiscent of a properly functioning Nafion membrane by being permeable to lithium ions and impermeable to polysulphide species.

The electrochemical activity of $LiMn_2O_4$ and polysulphide electrodes in 0.5 M Li_2SO_4 containing aqueous electrolyte are confirmed by means of cyclic voltammetry (CV) studies (Fig. S1). The two reversible redox peaks, reminiscent of the Li insertion-deinsertion processes in $LiMn_2O_4$ are clear seen at 0.68/0.82 and 0.76/0.90 V (vs SCE) on reduction and oxidation, respectively[21, 22]. For dissolved polysulphide solution, a single redox couple whose peak appeared at -0.3/-0.8 V (vs SCE) was detected in agreement with former studies[9, 23]. When the two electrodes operate in tandem in electrochemical cells (Fig. 2b) an average output voltage of nearly 1.5 V is measured. These cells deliver 110 mAh g^{-1} or 60 mAh g^{-1}, capacities at a 2 C (Fig. 2a) or at 10 C rate (Fig. S2), respectively, with excellent capacity retention. The reported capacity values herein refer to $LiMn_2O_4$ whose theoretical capacity is 148 mAh g^{-1}, thus, the capacity utilization is around 80% (at 2 C). The reason for such limitation comes from the use of a non-electrochemically optimized $LiMn_2O_4$ sample. We believe enhanced performances can be achieved with an optimised cathode material made by either with dual Al-F doping[24] or templating approaches[25].

Obviously, the cell voltage for this aqueous system (1.5 V) is lower than for classical Li-S batteries (2.2 V). Nevertheless, considering the lower initial cost (aqueous vs. organic electrolyte), ability to operate at superior current densities and anomalously high solubility of polysulphide salts in water (Li_2S not soluble in organics), the aqueous Li-ion/polysulphide battery stands a potential candidate to power stationary applications. Therefore, for this to happen, one must master the amount of gaseous product during cycling linked mainly to the polysulfide anolyte[13, 14].

As discussed in our former study[14], the electrochemical performance of sulphur (or its reduced polysulphide species) in aqueous media bears no similarities with the organic electrolyte counterparts as no reversible colour changes upon reduction/oxidation is observed. Instead, in aqueous electrolytes, the colour transforms from orange to greenish, and even disappears if the cells are not properly sealed[14] meaning that active material is prone to leave the cell via the formation of gaseous products. From the redox chemistry of polysulphides in aqueous media, three main chemical species are known to be formed, HS^-, S_x^{2-} and $H_2S(aq)$[8, 9, 26]. Thus, an over-simplified reaction mechanism can be written as in (Eq. 1).

$$S_2^{2-} + 2H_2O + 2e^- \leftrightarrow 2HS^- + 2OH^- \quad E_o = -0.51 \text{ V vs SHE} \qquad \text{(Eq. 1)}$$

In light of this remark, we avoid giving specific values for the theoretical capacity of our system as it will be highly depending on many parameters among which are the types of polysulphides, amount of conductive additives, pH, type of the cell compartment *etc*. Nevertheless, considering the use of K_2S at pH 14, we expect to have a specific capacity ranging from 240-480 mAh g^{-1}.

Turning to side reactions, according to Eq.1, gaseous products form and they seepage from the cell depending on its configuration. Fig. 3a shows the capacity behaviour of a cell whose balancing is done by taking into account the capacities of both polysulphide and $LiMn_2O_4$. As previously shown at Fig. 2a, a capacity of ~105 mAh g^{-1} is obtained for the first cycle but here the cell was dead after 60 cycles. Upon opening the cell we note that the characteristic colour of dissolved polysulphide was transformed from yellowish (Fig. 3a, inset picture) to a colourless/transparent solution (Fig. 3b, inset picture). When the same cell was restarted with additional polysulphide, there is an upgrading its capacity from ~10 mAh g^{-1} to ~80 mAh g^{-1} which is followed by a smooth and continuous capacity decrease. The lost in capacity (~105 to ~80 mAh g^{-1}) between the two events is indicative of the loss of an active material during cycling. Practically-wise, for large scale applications, this means that such an aqueous battery system will need to be couple with a tank accommodating large volume of dissolved polysulphide, so that the system as a whole can be viewed as an intermittent semi-redox flow set-up[5].

To understand the nature of the side products generated upon cycling, a home-made Swagelok cell connected to mass spectrometer was used. During such an in-situ cycling experiment, the release gaseous reaction products were continuously pumped off from the top of cell through a capillary into the mass spectrometer, and analysed/quantified on-line by detecting changes in mass signals as a function of time. The evolution of the gaseous products between the 1st and 30th cycles is shown in Fig. S3. The amount of O_2 release increases upon cycling, but to our surprise, the difference in the amount of release sulphur based gases products between the 1st and 30th cycles was barely detectable as exemplified by the tiny change of the H_2S (molecular weight: 34 g/mole) signal (Fig. S3). This could suggest that the formed corrosive H_2S is consumed during cycling which is supported by visual observation of corrosion pits at the surface of our stainless-steel current collector. Regarding corrosion, besides H_2S, one could also consider the role of Li_2SO_4 salt which is proven to result corrosion on the stainless steel electrode at the electrochemical capacitors in aqueous electrolytes[27].

Regenerative adsorption and removal of H_2S is part of many industrial processes, and this is mainly done via the use rare earth oxides[28], activated carbons[29] or porous silica[30]. Moreover, in the field of Li-S battery, oxygenated porous architectures have already been proposed to trap dissolved polysulphides[31, 32] due to its Si-O binding sides. So in light of this previous art we decide to use porous silica additives in order to adsorb sulphur-based products. Here we used, a SBA-15 mesoporous silica[20] with bi-connected porous structure and highly hydrophilic surface properties. It exhibits high surface area, 740 m^2/g, (Brunauer-Emmett-Teller) with a very narrow pore size distribution centred at 8.8 nm and a specific pore volume of 0.95cm^3/g (Fig. S4). HRTEM images (Fig. S5) reveals that SBA-15 silica comprises well-ordered hexagonal arrays of mesopores (1D channel) and a 2D hexagonal structure.

Electrochemical cycling experiments were carried out to investigate the influence of the SBA-15 additive. Fig. 4a shows the 3rd galvanostatic discharge/charge profiles recorded at a current rate of 2C with and without SBA-15 additives. The irreversible capacity for the cell containing SBA-15 is the lowest and this is most likely due to the great aptitude of SBA-15 silica to trapped H_2S. Moreover, the addition of SBA-15 (Fig. 4b) enables to obtain a batter capacity retention performance as sustained capacity retention of 90 mAh g^{-1} at 2 C up to 200 cycles could be achieved. Without SBA-15 we have a smooth increase in capacity up to 50 cycles follow by a severe downturn afterwards. This smooth increase is reminiscent of time-dependence electroactivation process which could here due to the time required to establish a good interaction between hydrophobic carbon and aqueous polysulfide. Lastly other oxides, besides SBA-115, having a great affinity towards sulphur, Ti_4O_7 as recently reported[33], could also enhance the cell performances.

4. Conclusions

Considering the low cost and long cycle life requirements from a large-scale storage, aqueous-based batteries are attractive. Herein, we have demonstrated the feasibility and proof of concept of aqueous electrolyte polysulphide system utilizing a renowned cathode material, $LiMn_2O_4$, together with dissolved polysulphide (anolyte) and a Nafion-based membrane as a separator. We show that such a 1.5 V battery system, free of costly and brittle ceramic membranes, provides promise to construct a long-lifespan storage device. Side issues such as the release of gaseous products (H_2S) were partially overcome via the use of porous SBA-15 silica adsorbent. Sustained reversible capacities of 90 mAh g^{-1} at 2 C rate for more than 200 cycles were already achieved. Although we have established proof-of-concept with Nafion, obvious improvements of this work range from, exploring other cationic polymer membranes besides Nafion as well as other oxides besides SBA-15 for H_2S trapping. Plus, to implement our general approach to Na-based systems will present much cost advantage options.

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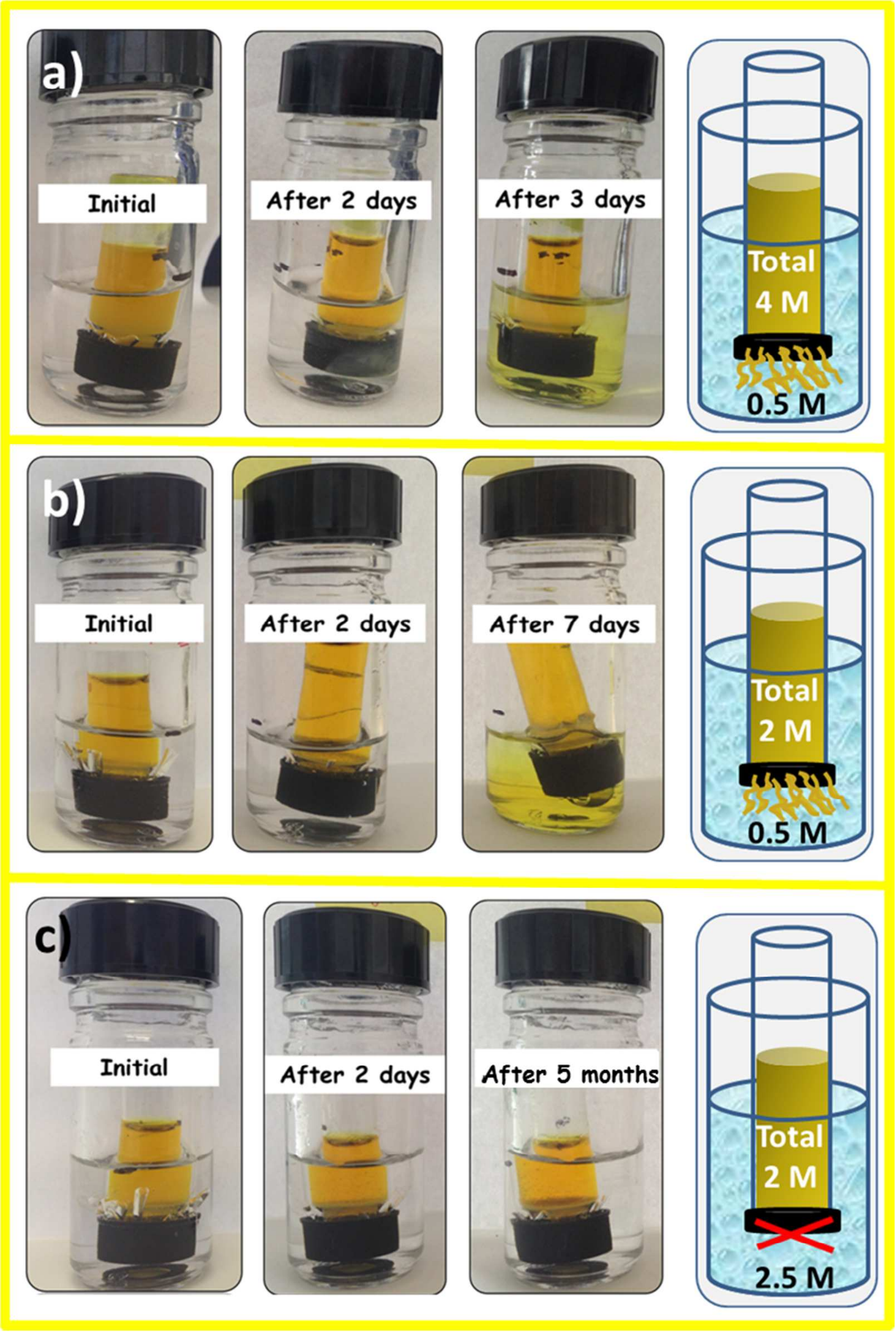

Fig. 1 Nafion membrane polysulphide leakage test with different salt concentrations after variable resting times a) 1.5 M polysulphide dissolved into a 2.5 M Li_2SO_4 aqueous electrolyte then placed into a 0.5 M Li_2SO_4 containing water, b) 1.5 M polysulphide dissolved into a 0.5 M Li_2SO_4 aqueous electrolyte then placed into a 0.5 M Li_2SO_4 containing water, c) 1.5 M polysulphide dissolved into a 0.5 M Li_2SO_4 aqueous electrolyte then placed into a 2.5 M Li_2SO_4 containing water. Note: only in the case of (c) inset and outside salt concentration is close to equilibrium resulting no leakage up to 5 months.

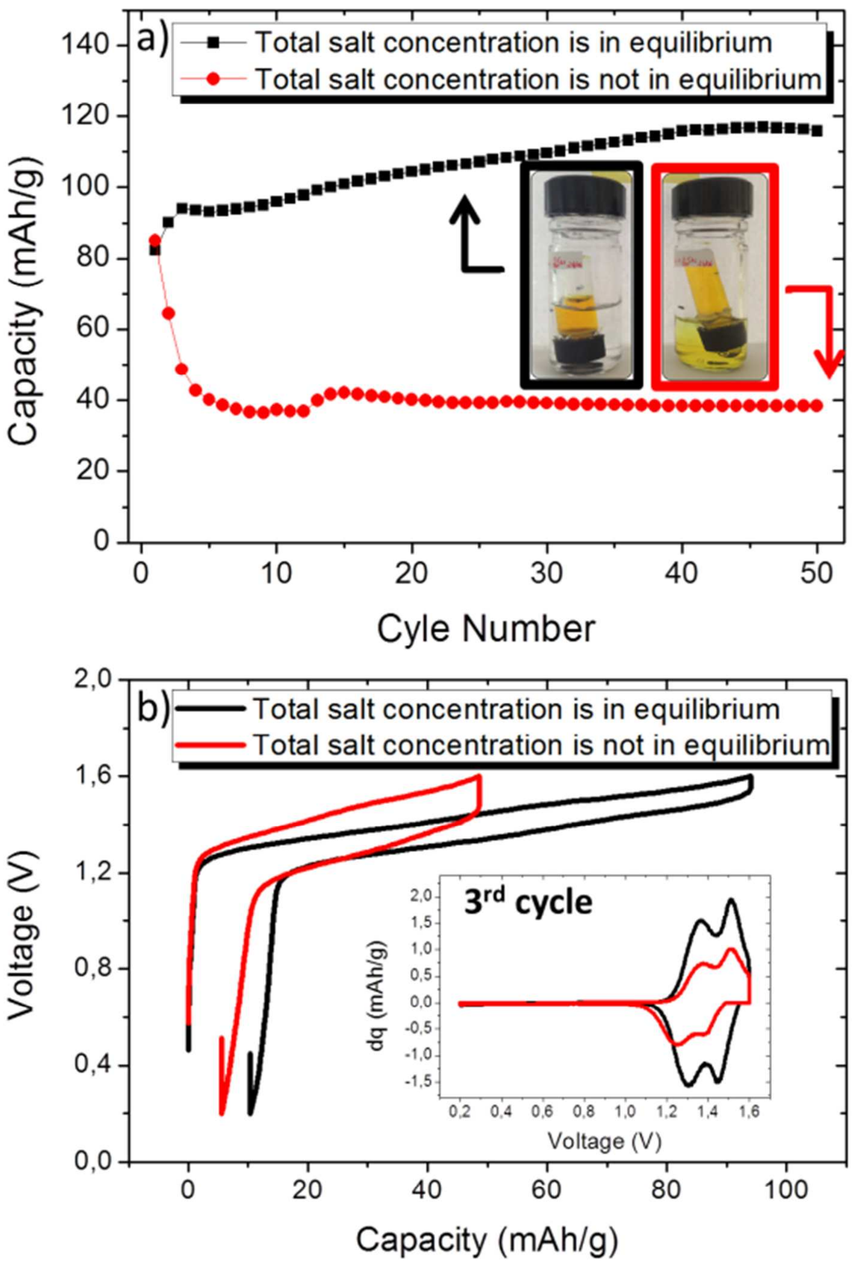

Fig. 2 a) Cycling performance of the aqueous electrolyte $LiMn_2O_4$-polysulphide cells at a 2 C current density. Capacity values refer to $LiMn_2O_4$ whose theoretical capacity is 148 mAh g^{-1}. Cell configuration at the black dots is 2.5 M Li_2SO_4 at $LiMn_2O_4$ cathode side and 0.5 M Li_2SO_4 containing polysulphide (1.5 M) at the anode side. Cell configuration at the red dots is 0.5 M Li_2SO_4 at $LiMn_2O_4$ cathode side and 0.5 M Li_2SO_4 containing polysulphide (1.5 M) at the anode side. Note: cells were not balanced and excess of polysulphide were used here ensuring to compensate the elimination of gaseous active material in the cell meaning that considering the theoretical capacity value of $LiMn_2O_4$ and dissolved polysulphide, the ration between cathode and anolyte is kept at 2.5. b) Third galvanostatic charge-discharge profiles of the $LiMn_2O_4$/polysulphide full cells with different electrolyte configuration at a current density of 2C for the voltage range between 0.2 and 1.6 V.

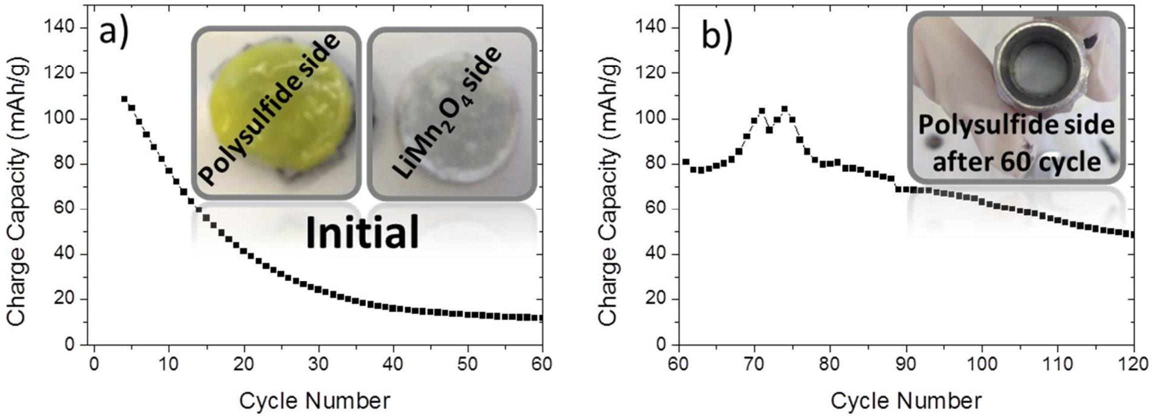

Fig. 3 a) Cycling performance of the aqueous electrolyte $LiMn_2O_4$-polysulphide cell at a 2 C current density. Cell balancing is done considering the theoretical capacity value of $LiMn_2O_4$ and dissolved polysulphide. Capacity values refer to $LiMn_2O_4$ whose theoretical capacity is 148 mAh g^{-1}. Cell configuration is 2.5 M Li_2SO_4 at $LiMn_2O_4$ cathode side and 0.5 M Li_2SO_4 containing polysulphide at the anode side. b) Cycling performance of the same cell (a) when it was restarted with additional polysulphide at a 2 C current density.

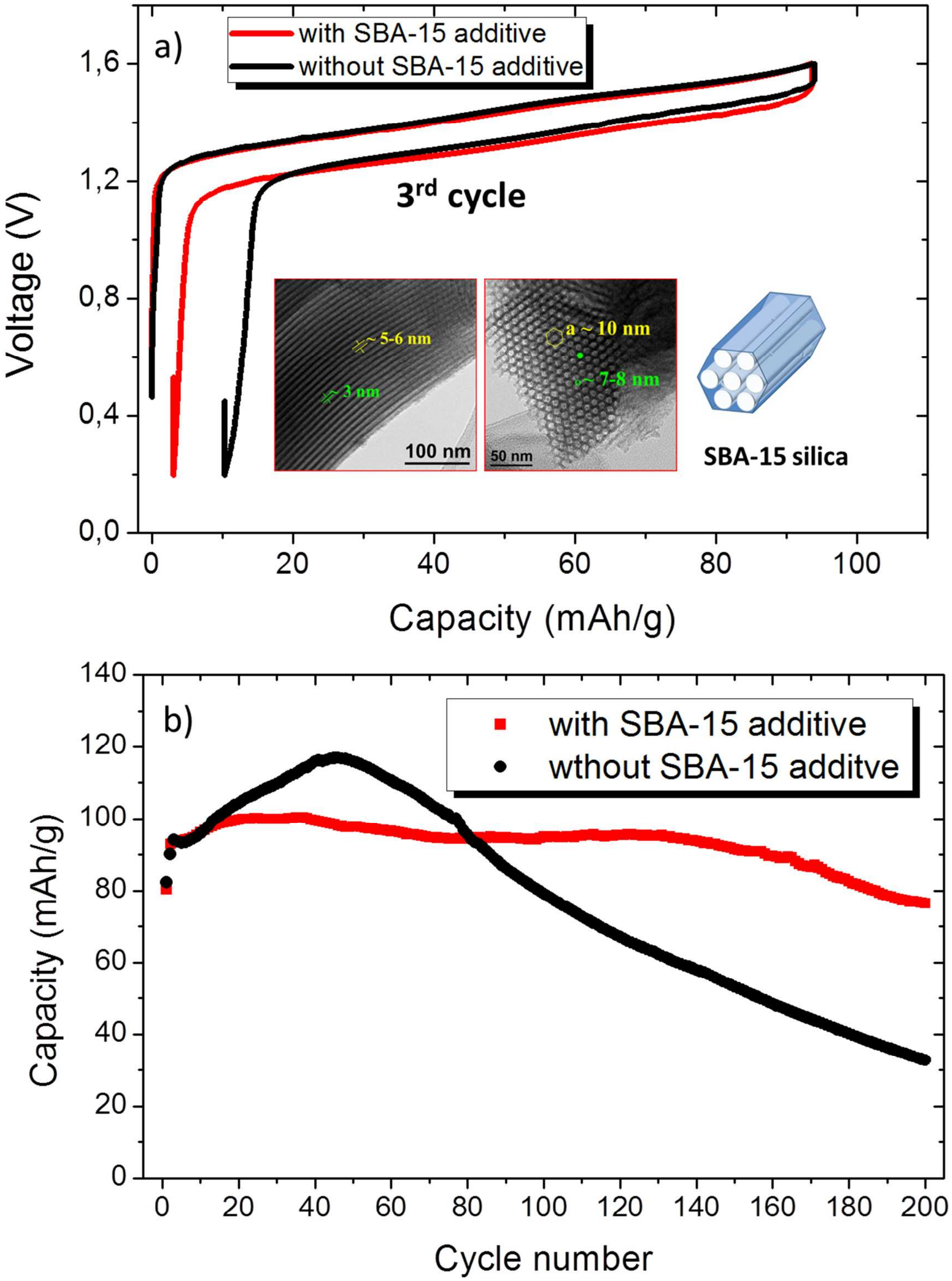

Fig. 4 a) Third galvanostatic charge-discharge profiles of the $LiMn_2O_4$/polysulphide full cells with (red) and without (black) SBA-15 additive at a current density of 2 C for the voltage range between 0.2 and 1.6 V, b) comparison of the cycling stability of the aqueous electrolyte $LiMn_2O_4$-polysulphide cells with (red) and without (black) SBA-15 additive at a 2 C current density. Capacity values refer to $LiMn_2O_4$ whose theoretical capacity is 148 mAh g^{-1}. Cell configuration in both cases are 2.5 M Li_2SO_4 at $LiMn_2O_4$ cathode side and 0.5 M Li_2SO_4 containing polysulphide (1.5 M) at the anode side.

References

1. H. L. Pan, Y. S. Hu and L. Q. Chen, *Energy & Environmental Science*, 2013, **6**, 2338-2360.
2. J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359-367.
3. W. Li, W. R. McKinnon and J. R. Dahn, *Journal of the Electrochemical Society*, 1994, **141**, 2310-2316.
4. L. Chen, Z. Y. Guo, Y. Y. Xia and Y. G. Wang, *Chemical Communications*, 2013, **49**, 2204-2206.
5. Y. H. Lu, J. B. Goodenough and Y. Kim, *Journal of the American Chemical Society*, 2011, **133**, 5756-5759.
6. Y. Zhao, L. N. Wang and H. R. Byon, *Nature Communications*, 2013, **4**.
7. Y. Zhao, Y. Ding, J. Song, L. L. Peng, J. B. Goodenough and G. H. Yu, *Energy & Environmental Science*, 2014, **7**, 1990-1995.
8. D. Peramunage and S. Licht, *Science*, 1993, **261**, 1029-1032.
9. S. Licht and D. Peramunage, *Journal of the Electrochemical Society*, 1993, **140**, L4-L6.
10. S. Licht, J. Manassen and G. Hodes, *Journal of the Electrochemical Society*, 1986, **133**, 272-277.
11. S. Licht and J. Manassen, *Journal of the Electrochemical Society*, 1985, **132**, 1076-1081.
12. S. Licht, *Solar Energy Materials and Solar Cells*, 1995, **38**, 305-319.
13. Y. S. N. S. J. Visco, B. D. Katz, L. C. De Jonghe, N. Goncharenko and V. Loginova, , *US Patent, US 2013/0122334*, 2013.
14. R. Demir-Cakan, M. Morcrette, J. B. Leriche and J. M. Tarascon, *Journal of Materials Chemistry A*, 2014, **2**, 9025-9029.
15. T. E. Springer, T. A. Zawodzinski and S. Gottesfeld, *Journal of the Electrochemical Society*, 1991, **138**, 2334-2342.
16. R. R. Garsuch, D. B. Le, A. Garsuch, J. Li, S. Wang, A. Farooq and J. R. Dahn, *Journal of the Electrochemical Society*, 2008, **155**, A721-A724.
17. H. Schneider, A. Garsuch, A. Panchenko, O. Gronwald, N. Janssen and P. Novak, *Journal of Power Sources*, 2012, **205**, 420-425.
18. Z. Jin, K. Xie, X. Hong, Z. Hu and X. Liu, *Journal of Power Sources*, 2012, **218**, 163-167.
19. I. Bauer, M. Kohl, H. Althues and S. Kaskel, *Chemical Communications*, 2014, **50**, 3208-3210.
20. D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548-552.
21. C. Wessells, R. Ruffo, R. A. Huggins and Y. Cui, *Electrochemical and Solid State Letters*, 2010, **13**, A59-A61.
22. H. Schlorb, M. Bungs and W. Plieth, *Electrochimica Acta*, 1997, **42**, 2619-2625.
23. J. Shao, X. Y. Li, L. Zhang, Q. T. Qu and H. H. Zheng, *Nanoscale*, 2013, **5**, 1460-1464.
24. G. Amatucci, A. Du Pasquier, A. Blyr, T. Zheng and J. M. Tarascon, *Electrochimica Acta*, 1999, **45**, 255-271.
25. W. Tang, Y. Y. Hou, F. X. Wang, L. L. Liu, Y. P. Wu and K. Zhu, *Nano Letters*, 2013, **13**, 2036-2040.
26. D. J. Obrien and F. B. Birkner, *Environmental Science & Technology*, 1977, **11**, 1114-1120.
27. P. Ratajczak, K. Jurewicz and F. Beguin, *Journal of Applied Electrochemistry*, 2014, **44**, 475-480.
28. M. Flytzani-Stephanopoulos, M. Sakbodin and Z. Wang, *Science*, 2006, **312**, 1508-1510.
29. F. Adib, A. Bagreev and T. J. Bandosz, *Environmental Science & Technology*, 2000, **34**, 686-692.
30. G. Q. Liu, Z. H. Huang and F. Y. Kang, *Journal of Hazardous Materials*, 2012, **215**, 166-172.
31. R. Demir-Cakan, M. Morcrette, F. Nouar, C. Davoisne, T. Devic, D. Gonbeau, R. Dominko, C. Serre, G. Ferey and J.-M. Tarascon, *Journal of the American Chemical Society*, 2011, **133**, 16154-16160.
32. X. L. Ji, S. Evers, R. Black and L. F. Nazar, *Nature Communications*, 2011, **2**.
33. D. K. Q. Pang, M. Cuisinier, and L. F. Nazar *Nature Communications*, 2014.