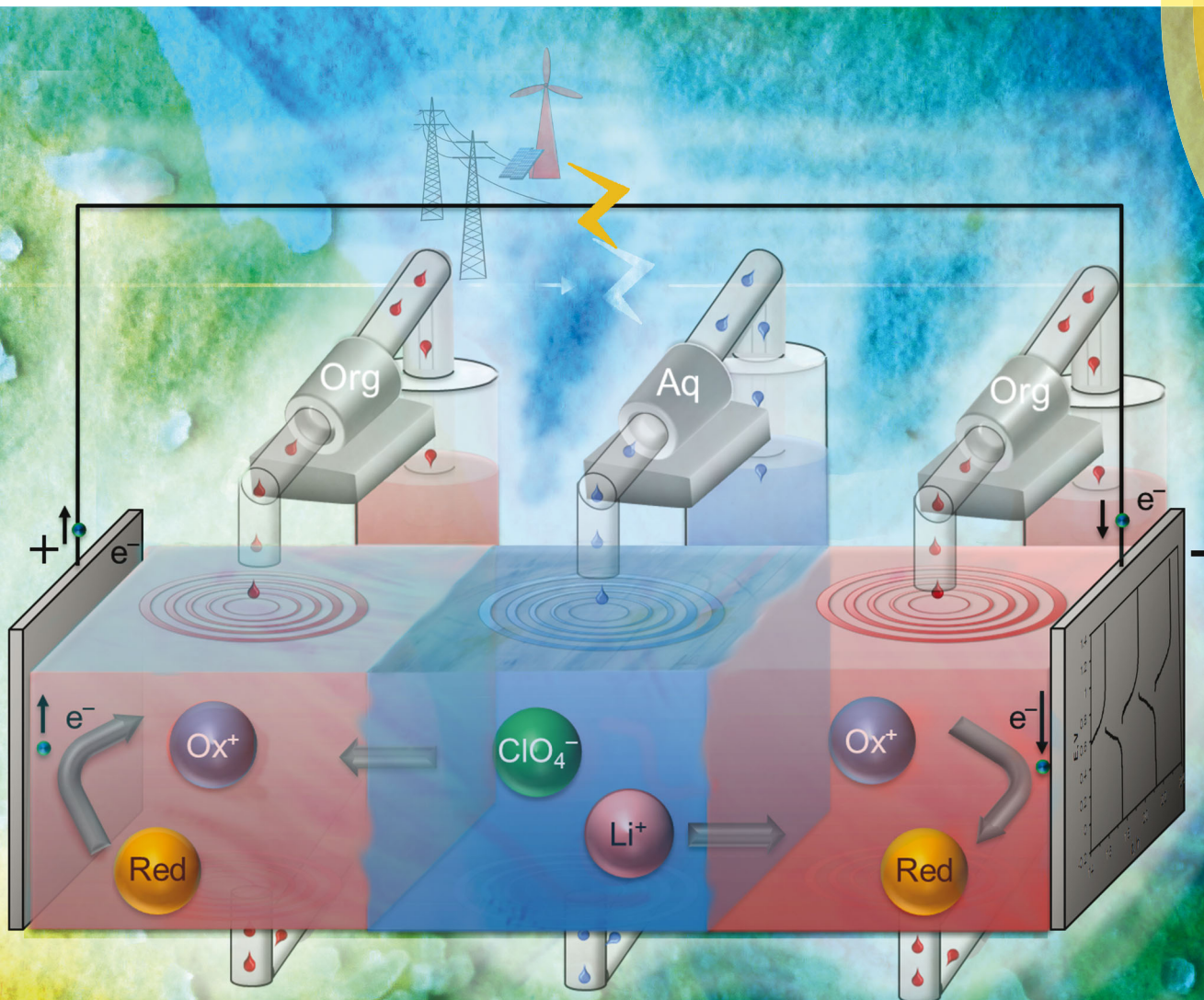


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ISSN 1359-7345



COMMUNICATION

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175 YEARS



Cite this: *Chem. Commun.*, 2016, 52, 9761

Received 23rd May 2016,
Accepted 14th June 2016

DOI: 10.1039/c6cc04325a

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Ion transfer battery: storing energy by transferring ions across liquid–liquid interfaces†

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A battery utilizing the Galvani potential difference between aqueous and organic phases is demonstrated. The battery consists of two organic redox electrolytes separated by an immiscible aqueous phase. The charge is stored by transferring a salt from the aqueous phase into organic phases in ion transfer coupled electron transfer reactions.

To prepare a battery, two redox couples with sufficient potential difference are required.^{1,2} In a typical battery, this potential difference is due to the difference in the redox potentials of the redox couples. But it is also possible to construct a battery by utilizing the Galvani potential difference between two phases. For example, in batteries, the potential difference between the two electrodes stems from the different Fermi levels of the electrons for the two redox couples (the Fermi level of the electron in a solution is equal to the redox potential of the redox species expressed on an energy scale and the Galvani potential of the solution: $E_F = -e(E_{O/R} + \phi)$).³ In a typical redox flow battery, the Galvani potential of the electrolytes is almost constant, and almost all the potential difference is due to the differences in the redox potentials of the two electrolytes. But here, we demonstrate a battery where most of the potential difference is actually due to the Galvani potential difference between the two electrolytes.

Since the pioneering work of Gavach,^{4–6} and Koryta and Samec *et al.*,^{7,8} ion transfer reactions at the interfaces between two immiscible electrolyte solutions (ITIES) have become an integral part of electrochemistry.^{9–11} The Galvani potential difference between the two phases can be controlled electrochemically by an external power supply, or chemically by the partitioning of ions between the two phases.^{9–11} Ion transfer reactions have also been studied with droplet-modified electrodes,

where a redox reaction at an electrode covered by a droplet induces an ion transfer reaction across the interface between the droplet and the surrounding phase. In this case, the measured redox potential depends strongly on the transferring ion.^{12–14} In this communication, we demonstrate a battery utilizing decamethylferrocene (DMFc) as a redox molecule in the organic phases, separated from each other by an aqueous phase, forming two liquid–liquid interfaces in series, as shown in Fig. 1. These interfaces are polarized with different common ions, resulting in a secondary battery with a cell voltage of up to 0.8 V. In effect, the battery stores charge by transferring a salt

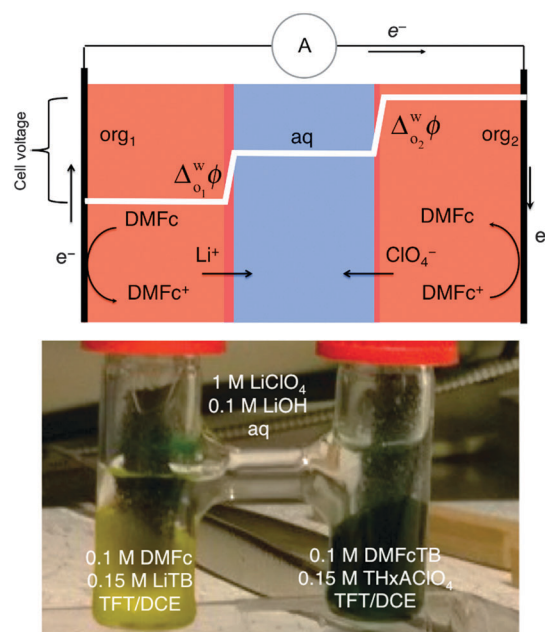


Fig. 1 Battery reactions upon discharge and the illustration of the Galvani potential profile in the cell (top), and a figure showing the realization of the battery and the composition of the electrolytes in the fully charged state (bottom). The two organic redox electrolytes are separated by an immiscible aqueous phase.

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† Electronic supplementary information (ESI) available: Experimental methods. See DOI: 10.1039/c6cc04325a

from the aqueous phase to the oil phases. The advantage of the present system is that both redox reactions of the $\text{DMFc}^+/\text{DMFc}$ couple and the ion transfer reactions are very facile and reversible, requiring less overpotential, while the system does not require any ion exchange membranes or separators. The cycling of the battery takes place with a good coulombic efficiency of *ca.* 100% and energy efficiencies up to 80%, but the cycling stability is limited by the evaporation of the solvents.

The operating principle of the battery is illustrated in Fig. 1. During discharge, DMFc is oxidized to DMFc^+ on the negative electrode and DMFc^+ is reduced to DMFc on the positive electrode, while the lithium and perchlorate ions are transferred from the electrolytes to the aqueous solution, ensuring the electroneutrality of the electrolytes, in two ion transfer coupled electron transfer reactions.

The reactions occurring at the positive and negative electrodes were investigated outside the glove box by cyclic voltammetry. Cyclic voltammograms obtained with 1,2-dichloroethane (DCE) droplet modified carbon paste electrodes immersed in aqueous LiClO_4 solution are displayed in Fig. 2A and B, with half-wave potentials of -0.70 V and -0.12 V *vs.* $\text{Ag}/\text{AgCl}/(3 \text{ M KCl})$ for the $\text{DMFc}^+/\text{DMFc}$ couple with lithium tetrakis pentafluorephenyl

borate (LiTB) and tetrahexylammonium perchlorate (THxAClO_4) in the DCE droplet, respectively.

The peak currents depend linearly on the square root of the scan rate, due to the mass transport of the $\text{DMFc}^+/\text{DMFc}$ couple in the organic droplet. The solubility of DMFcTB (synthesized as described previously)¹⁵ in a 100 mM LiTB solution of DCE could be estimated to be *ca.* 40 mM considering that the diffusion coefficient of DMFc^+ is equal to the diffusion coefficient of DMFc . The reduction peak current is always slightly higher than the oxidation peak, indicating that some of the DMFc generated at the electrode during the reduction is oxidized by oxygen (catalyzed by the transferred hydrated lithium ions^{16,17}). These CVs demonstrate that a battery with a cell voltage of more than 0.8 V can be constructed using this concept. The Fermi level of the electron for the redox couple depends on both the Nernst potential of this redox couple and the Galvani potential difference. The interface at the negative electrolyte is polarized by Li^+ as the common ion, resulting in $\Delta\phi^w$ of *ca.* 0.55 V, while the other interface is polarized by the partition of ClO_4^- resulting in $\Delta\phi^w$ of *ca.* -0.2 V, (calculated as described for example in ref. 18 and 19).

Utilizing a more hydrophilic anion than perchlorate would increase the voltage of the battery. For example, replacing the perchlorate with chloride would shift the wave by *ca.* 0.3 V to more positive potentials. However, the chosen anion should transfer at higher potentials than DMFc^+ , otherwise DMFc^+ could be transferred to the aqueous phase instead of the transfer of the anion from aqueous to oil phase upon charging the battery (for example, see ref. 18). Hence, perchlorate was chosen for the subsequent battery studies. The choice of solvent is also important for the battery. The solvent should be only slightly miscible with water, but should have high enough polarity to allow the dissolution of the supporting electrolyte. For example, typical solvents like acetonitrile and propylene carbonate could not be used, as they show no potential window for liquid-liquid electrochemistry. Alternatively, redox ionic liquids could be considered. In this study, two solvents typically utilized in this field, DCE and trifluorotoluene (TFT), were used for battery studies.¹¹ These solvents have a polarizable potential window of *ca.* 0.7²⁰ and 1.0 V,¹⁹ respectively. Another important factor is the solubility of the components. Both LiTB and THxAClO_4 were found to be sufficiently soluble in the organic phase, at least up to 150 mM concentration, and 100 mM of DMFc could be easily dissolved in both DCE and TFT. Unfortunately, the solubility of the DMFcTB was a limiting factor, so saturated solutions of DMFcTB were used for battery experiments.

The electrochemical performance of the battery was tested in a static H-cell configuration under anaerobic conditions, with porous reticulated vitreous carbon electrodes (or GC electrodes, 3 mm diameter) on both sides, in a two-electrode set-up, with both DCE and TFT as the organic phases, under vigorous stirring. The cell composition and the reactions upon discharge for the ion transfer battery are depicted in Fig. 1. As the organic solvent has low conductivity, most of the electrochemical reactions take place close to the three-phase boundary between the ITIES and the electrode.

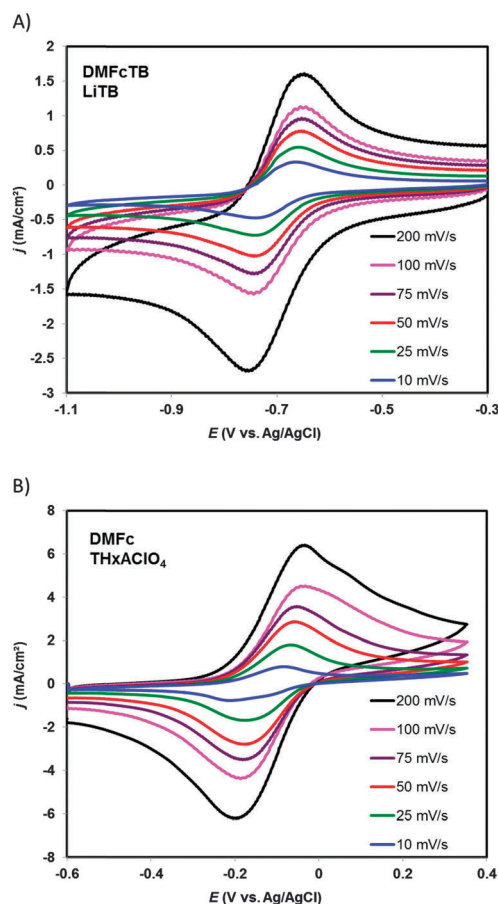


Fig. 2 (A and B) Cyclic voltammograms of droplet-modified electrodes (DCE solution containing (A) 150 mM LiTB and a saturated solution of DMFcTB , and (B) 150 mM THxAClO_4 and 100 mM DMFc) immersed in an aqueous 1 M LiClO_4 and 100 mM LiOH solution.

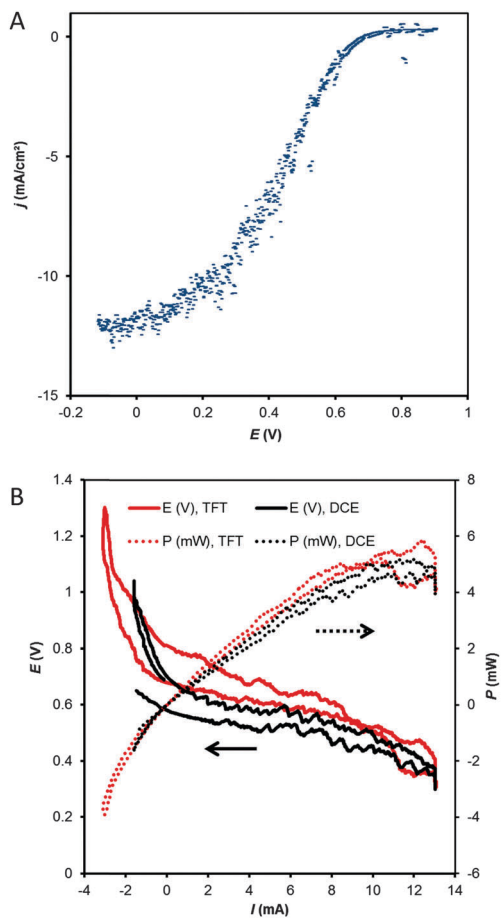


Fig. 3 (A) *IR* compensated CV measurements of the battery described Fig. 1 (with DCE) under stirring with GC electrodes (radius 1.5 mm). (B) *IR* compensated polarization and power curves of the battery obtained from CV measurements under stirring with RVC electrodes. $R = 290 \, \Omega$ for DCE and $R = 300 \, \Omega$ for TFT.

Fig. 3A shows the *IR* compensated CV of the fully charged battery with glassy carbon disc electrodes (radius 1.5 mm) in both electrolytes, enabling the accurate estimation of the current densities. The battery is able to produce current densities comparable to typical redox flow batteries, even at this low concentration of redox mediators. To perform cycling experiments in a shorter time, porous high surface area carbon electrodes were used instead. Fig. 3B shows the polarization curves and the power output of the battery using DCE and TFT as organic solvents with high surface area electrodes. The hysteresis observed in the CVs indicates that the convection in the cell was insufficient to achieve steady state conditions with RVC electrodes. The maximum power is reached in both cases for a current value of around 10 mA. The battery performance is slightly better with TFT. This is because the energies required to transfer Li^+ and ClO_4^- from water to TFT are higher than from water to DCE, resulting in a higher cell voltage.

The example of the cycling behavior of the battery is shown in Fig. 4A, while the cycling performance of the battery is depicted in Fig. 4B and C with DCE and TFT as organic solvents, respectively. In both cases, the battery performance improved

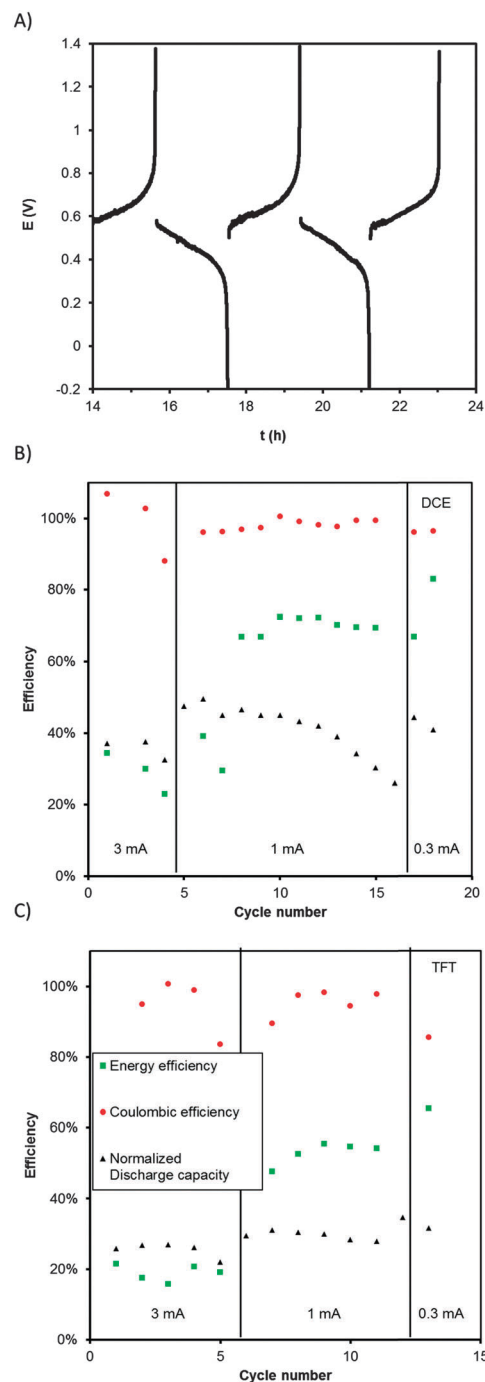


Fig. 4 (A) Example for the *IR* corrected cycling behavior with DCE as the solvent at 1 mA. (B and C) Coulombic and energy efficiencies (*IR* corrected) and the normalized discharge capacities at different charge and discharge currents with DCE (B) and TFT (C).

with decreasing currents. The energy efficiency increased significantly, and reached 83% at 0.3 mA in DCE and 65% in TFT. With DCE, the energy efficiency is higher than with TFT, but the normalized charge capacity tends to decrease after several cycles, while it is more stable in TFT. This may be due to the fact that as DCE evaporated, the concentration of the active species increased up to its saturation limit and thus the theoretical

capacity decreased. The normalized capacity was calculated assuming full utilization of 100 mM of the redox mediator. However, the true available capacity was lower due to the low solubility of DMFcTB. As the normalized capacities were lower in TFT, this indicates that the solubility limit of DMFcTB was lower than in DCE. However, as discharge capacities of over 50% are obtained while the solubility of the DMFcTB is only 40 mM, some of the initially solid DMFcTB dissolves during discharge and participates in the electrochemical reaction.

In both cases the battery had difficulties in starting the discharge at the highest current (3 mA), with the potential dropping close to zero to initiate the discharge. At lower currents (1 mA and 0.3 mA), the cycles of charge and discharge are more stable. After each cycle of charge or discharge, the ohmic loss in the cell was measured by fast chronopotentiometry. It seems to vary slightly due to the changes in the position of the liquid–liquid interface. Unfortunately, the battery performance was not very stable due to the solvent evaporation (and possibly also electrochemical solvent decomposition). Also, in some cases the cell geometry was not sufficient to keep the organic phases completely separate. The structure of the organic phase containing LiTB changed drastically to behave more like an emulsion and increased its volume, leading to occasional leaks into the other compartment. This kind of leakage terminated the cycling of the battery with TFT after the 2nd cycle at 0.3 mA current, but these results demonstrate the concept.

In short, we have demonstrated the concept of utilizing the Galvani potential difference between aqueous and organic phases to realize a battery, where the charge is stored in transferring a salt from an aqueous phase to an organic phase in an ion transfer coupled electron transfer reaction. A cell voltage of 0.8 V is demonstrated by utilizing LiClO₄ as the transferring salt from the water phase to trifluorotoluene phases. The cycling of the battery takes place with a good Coulombic efficiency close to 100% and energy efficiencies up to 80%, but the cycling stability is limited. However, the high ohmic drop in the organic phases, introduction of flammable organic solvents into the flow battery, and the unsatisfactory battery performance renders the demonstrated system unpractical. To improve the concept further, a flow battery system with droplets of the organic phase in the aqueous flow could be envisaged. This would drastically reduce the cell resistance and significantly increase the area between the organic and aqueous phases, although a separator would be required. The system with redox polymers in the organic phase could also be envisaged, allowing utilization of more hydrophilic anions like Cl[−] instead of the perchlorate, increasing the cell voltage.

Additionally, utilizing different redox mediators would increase the cell voltage. In this case, the Galvani potential difference would enhance the cell voltage. Possible candidates include all the redox couples commonly utilized in non-aqueous redox flow batteries as reviewed for example in ref. 1 and 21. Another interesting concept would be to use Galvani potential differences to boost the cell voltage of aqueous supercapacitors or batteries by introducing an organic phase between the two electrodes. In this case the system can provide a higher cell voltage, but suffers from an increased resistance.

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