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Published in:
Electrochimica Acta

DOI:
[10.1016/j.electacta.2019.134704](https://doi.org/10.1016/j.electacta.2019.134704)

Published: 20/10/2019

Document Version
Peer reviewed version

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Please cite the original version:
Zanzola, E., Gentil, S., Gschwend, G., Reynard, D., Smirnov, E., Dennison, C. R., Girault, H. H., & Peljo, P. (2019). Solid electrochemical energy storage for aqueous redox flow batteries: The case of copper hexacyanoferrate. *Electrochimica Acta*, 321, [134704]. <https://doi.org/10.1016/j.electacta.2019.134704>

Solid electrochemical energy storage for aqueous redox flow batteries: the case of copper hexacyanoferrate

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Keywords: aqueous organic redox flow batteries, solid charge storage material, redox mediator, Prussian blue analogue

Abstract

All redox flow batteries suffer from low energy storage density in comparison with conventional Li-ion batteries. However, this issue can be mitigated by utilization of solid energy storage materials to enhance the energy storage capacity. In this paper we demonstrate the utilization of copper hexacyanoferrate (CuHCF) Prussian blue analogue for this purpose, coupled with N,N,N-2,2,6,6-heptamethylpiperidinyloxy-4-ammonium chloride (TEMPTMA) as a soluble redox mediator to target the redox transitions of the solid material. In this case, indirect charging and discharging of a solid material suspended in the electrolyte by electrochemically oxidized/reduced TEMPTMA was observed by chronoamperometry. Secondly, electrochemistry of different CuHCF composites with carbon black and multi-walled carbon nanotubes investigated, highlighting that the high conductivity of the solid energy storage materials is crucial to access the maximal charge storage capacity of the solid material. Finally, a CuHCF-TEMPTMA/Zn aqueous redox flow battery achieved stable cycling performances with high coulombic efficiency of 95% and volumetric capacity of 350 C mL⁻¹.

1 Introduction

Electrochemical energy storage (EES) is key to the integration of renewable energy sources in the electric grid and to promote an energy transition towards a carbon-neutral society.^{1,2} EES systems improve the grid reliability and utilization by acting as a buffer for the intermittent energy production in different roles, ranging from frequency regulation to peak shaving and load shifting.³ Among several EES technologies, redox flow batteries (RFBs) store energy in two soluble redox couples contained in separate tanks, allowing a decoupling of the battery's power from the energy storage.⁴ The simplicity in terms of electrochemical reactions, the scalability and the flexibility make RFBs suitable for stationary storage applications. In comparison with common rechargeable batteries, it suffers from low energy densities of approximately 25-40 Wh L⁻¹, constrained by the solubility limit of redox-active species from 1 to 3 M. To circumvent this limitation, semi-solid flow batteries, developed by Duduta *et al.* in 2011, flowed highly concentrated (10 to 40 M) lithium ion intercalation materials as a slurry.⁵ However, this approach requires the use of highly conducting additives, leading to complex fluid dynamics and drop of the volumetric energy density.⁶⁻⁸

Alternatively, Wang *et al.* studied in 2006 the so-called redox-targeting flow battery that combines the concept of charge storage of solid batteries and the electrochemical properties of soluble redox species.⁹ Typically, the insoluble solid energy storage material (LiFePO₄) is stored in the electrolyte composed of a Li-salt and one or more soluble redox active molecules acting as 'redox mediators'. If two redox mediators are used, the solid material should have a formal redox potential in between. For a single redox mediator, a close agreement between the formal potentials of the solid and soluble species is essential to allow a sufficient driving force for the solid-liquid interfacial charge transfer process. This approach allows to significantly increase the energy storage capacity and also enhances the voltage efficiency due to the decreased concentration polarization.¹⁰ From 2010, this approach was successfully applied to non-aqueous Li¹¹⁻¹³ and Li-O₂^{14,15} RFBs using two active species to bracket the electrochemical lithiation/delithiation of the storage material. This concept is actually similar to the dual-circuit flow battery system developed by the Girault's group, where hydrogen and oxygen are produced in a chemical discharge reaction of a flow battery.^{16,17}

To overcome the disadvantages of the non-aqueous flow batteries, an aqueous redox-mediated flow battery operating at acidic pH was proposed by Girault's group with polyaniline (PANI) employed as a charge storage solid material for the positive side, with $\text{Fe}^{3+/2+}$ as the soluble redox mediator. The system exhibited a specific capacity of 64.8 mAh g^{-1} at a current density of 38.5 mA cm^{-2} , which represented a 3-fold improvement compared to the electrolyte alone (26.8 mAh L^{-1} at the same current density).¹⁸ Recently, Wang *et al.* have also demonstrated two aqueous systems based on redox-targeting flow battery concept.^{13,19}

On the other hand, for example Aziz *et al.*^{19–21} and Schubert *et al.*^{22–24} have demonstrated highly efficient organic alkaline and neutral RFBs with performances similar to the vanadium systems. They used organic redox couples such as 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), viologen or quinone derivatives at concentration ranges from 1 to 2 M. However, these systems still suffer from low energy storage density. Therefore, addition of solid electrochemical energy-storage materials appear to be highly desirable to realize large-scale stationary energy-storage systems.

Solid candidates include typical cation intercalation materials developed for aqueous Li/K/Na *etc.* ion batteries. One promising class of candidates are the Prussian blue analogues, as they display reasonable high rate capability and good stabilities^{25–27}, as demonstrated in solid batteries^{28–31} or supercapacitors.³² These materials have applications in electrochemical sensors, electrocatalysis, photocatalysis, and electrochromism.³³ All these applications are a result of the redox activity of the transition metal, coupled with ion-exchange properties allowing fast intercalation of hydrated ions.

In the present work, copper hexacyanoferrate (CuHCF),^{35,36} a Prussian blue analogue, was investigated as a low cost solid storage material in 1 M potassium chloride solution. Indeed, CuHCF has an open framework, which allows hydrated K^+ or Na^+ intercalation/deintercalation mechanism. Recently, this molecule demonstrated long-life cycling (83% capacity retention after 40000 cycles) at a 17 C-rate between 0.8 and 1.2V *vs* SHE in 1 M KNO_3 .³⁷ In addition, *N,N,N*-2,2,6,6-heptamethylpiperidinyloxy-4-ammonium chloride (TEMPTMA), a highly water soluble and electroactive organic radical, was used as redox mediator to match the formal potential of the CuHCF in the positive side of an aqueous organic redox flow battery.

More specifically, TEMPTMA-mediated electron transfer at the liquid-solid interface of pristine and carbon-coated CuHCF and K^+ -intercalation mechanisms were investigated by

electrochemical analysis, along with density functional theory calculations and finite element simulations.

2 Experimental Protocol

2.1 Materials and Methods

Copper nitrate trihydrate ($(\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O})$, puriss. p.a. 99%), 1-Methyl-2-Pyrrolidone, (NMP, reag. grade 99%), Acetone (CH_3COCH_3 , puriss. p.a. ACS, reag, reag ISO, reag. Ph. Eur $\geq 99.5\%$) Potassium chloride (KCl, ACS reagent, 99-100%), 4-dimethylamino-2,2,6,6 tetraethyl piperidine (96%), methyl iodide (CH_3I , contains copper as stabilizer, Reagent Plus, 99%) were purchased from Sigma-Aldrich. Potassium ferrocyanide trihydrate ($\text{K}_3\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, 99+% for analysis), N,N-dimethylformamide (DMF, $\geq 99.5\%$) were purchased from Acros Organics. Multi-walled carbon nanotubes (MWCNT, purity $> 98\%$, Outer Diameter 20-30 nm, length 0.5-2 μm) were purchased from Carbon Nanotubes Plus. Carbon black acetylene (CB, 99.99%, 50% compressed, average particles size 0.042 μm) was purchased from Strem Chemicals. Polyvinylidene fluoride (PVDF) was purchased from ABCR. Anion exchange resin (analytical grade anion exchange resin, AG[®] I-X8, 50-100 mesh, chloride form, Bio-Rad laboratories, Dowex) was purchased from Dow Chemical Co. All solvents and reactants were utilized without any further purification.

Potassium chloride (KCl, ACS reagent, 99-100%, Sigma Aldrich) aqueous solutions were used as electrolyte and prepared at different concentrations using Milli-Q water. A Millipore filtration system (Merck Millipore, Billerica, MA) was used to generate ultrapure water (18.2 $\text{M}\Omega \text{ cm}^{-1}$), from which all aqueous solutions were prepared. The pH was measured with a 744 pH meter Ω (Metrohm, Switzerland) and found to be 5.55 at 23.5 °C.

Electrochemical characterizations were performed with a SP-300 101 potentiostat from Bio-Logic (France) in a three-electrode setup. The working electrode was a glassy carbon electrode (GCE glassy carbon electrode OD: 6 mm ID: 3 mm, BAS Inc., Japan). A platinum wire (2 cm of length) was used as counter electrode and Ag/AgCl in 3 M KCl as reference electrode. PXRD pattern of as-synthesized CuHCF sample was recorded by Bruker diffractometer with Cu K_α non-monochromic irradiation ($\lambda = 1.5406 \text{ \AA}$), operated at 40 kV and 40 mA. Scanning electron microscopy (FEI SEM Teneo) was performed at 1-5kV, 0.12-1pA with lower in-lens and in-column detectors. X-ray photoelectron spectroscopy (VersaProbe II from Physical Electronics) was used to characterized the ex-situ composite.

2.2 Synthesis

Synthesis of copper hexacyanoferrate Prussian blue analogue

Copper hexacyanoferrate pristine powder was synthesized by simultaneous addition of 120 mL of 0.1 M copper (II) nitrate trihydrate and 120 mL of 0.05 M potassium ferrocyanide trihydrate to 60 mL of Milli-Q water upon vigorous and constant stirring.³⁸ The so-obtained solution was centrifuged for 30 minutes for three times and then the obtained suspension was allowed to rest for six hours. Then, the formed precipitate was filtered, washed with Milli-Q water and finally dried under vacuum at room temperature overnight.

Synthesis of *N,N,N*-2,2,6,6-heptamethylpiperidinyl oxy-4-ammonium chloride (TEMPTMA)

4.96 g (29 mmol) of 4-dimethylamino-2,2,6,6 tetraethyl piperidine was suspended in a first aliquot of 20 mL of acetone under vigorous agitation. 10 mL of methyl iodide was added into the mix followed by a second aliquot of 20 mL of acetone.²⁴ The reaction mixture was stirred at 60 °C for 20 hours to form *N,N,N*-2,2,6,6-heptamethylpiperidinyl oxy-4-ammonium iodide (**1**). The resulting mix was cooled down to room temperature and the suspended solid was collected by vacuum filtration. The solid was rinsed three times with 100 mL of acetone and then dried in the oven for two hours at 80 °C. Yield (**1**): 2.08 g (42%) of fine yellow powder. This material was treated with an anion exchange resin to exchange iodide into chloride by stirring an aqueous solution of (**1**) (2.08 g of (**1**) in 30 mL of Milli-Q water with an ion-exchange resin (*ca.* 10 g) for 24 hours at room temperature. The resulting solution was filtered to remove the ion exchange resin, which was then rinsed 2 times with 5 mL of Milli-Q water. The yellow aqueous filtered solution was collected and evaporated *in vacuo* to give pure *N,N,N*-2,2,6,6-heptamethylpiperidinyl oxy-4-ammonium chloride (**2**). The collected yellow powder was dried in the oven at 80 °C overnight. Yield (**2**): 90%. The absence of iodide was confirmed by cyclic voltammetry.

Ex-situ synthesis of the MWCNT-CuHCF composite for drop-casting onto glassy carbon electrode

70 mg of MWCNT were sonicated for 1 h in 150 mL of DMF in order to obtain a homogeneous black suspension. Then, 30 mg of CuHCF was added to the MWCNT dispersion. The dark

suspension was stirred for 24 hours at 80 °C under nitrogen and then filtered onto polytetrafluoroethylene filters (PTFE, Omnipore membrane filters, 0.45 µm JH, Merck Millipore Ltd). The obtained black powder was then dried under vacuum in order to remove any traces of DMF.

Ex-situ synthesis of the MWCNT-CuHCF composite for redox flow battery

10 mg of MWCNT were sonicated for 1 h in 70 mL of DMF in order to obtain a homogeneous black suspension. Then, 90 mg of CuHCF was added to the MWCNT dispersion. The dark suspension was stirred for 24 hours at 80 °C under nitrogen and then filtered onto polytetrafluoroethylene filters (PTFE, Omnipore membrane filters, 0.45 µm JH, Merck Millipore Ltd). The obtained black powder was then dried under vacuum.

2.3 Ink formulations for the electrochemical characterization

Table 1 summarizes the composition of each ink. All of them were sonicated for 30 minutes in NMP as solvent. 8µL of the final dispersion was then drop-casted onto a glassy carbon electrode (GCE glassy carbon electrode OD: 6 mm ID: 3 mm, BAS Inc., Japan) and allowed to dry under vacuum for 30 minutes in order to obtain a homogeneous film. The modified-GCE was then characterized by electrochemistry.

Table 1: Inks formulation used for the electrochemical characterizations.

Inks	MWCNT (mg)	Carbon Black (mg)	CuHCF (mg)	NMP (mL)
MWCNT	5.3	-	-	0.1
Carbon black	-	5.3	-	1
CuHCF	-	-	3	1
CB-CuHCF (30-70) wt%	-	0.9	2.1	1
CNT-CuHCF (30-70) wt%	0.9	-	2.1	1

2.4 Electrochemical characterization

Cyclic voltammetry (CV) was performed in 1 M KCl solution as supporting electrolyte in the presence of nitrogen. Galvanostatic cycling was performed in 1 M KCl as supporting electrolyte in the presence of nitrogen at different current values. Cut-off potentials of + 1.10 and + 0.41V vs SHE were applied for the charge and discharge processes, respectively.

2.5 Flow battery experiments

Chronoamperometry was performed in an H-cell shaped separated by a porous glass frit of 3 cm². Reticulated vitreous carbon pieces (RVC, 1 cm × 1 cm × 2 cm, 45 pores per inch) were used as working and counter electrodes. The battery experiments were performed using a three-electrochemical cell setup. The working electrode was connected onto the positive side, the counter electrode onto the negative side and an Ag/AgCl (KCl 3M) was used as reference electrode to follow the electrochemical reaction at the positive side. The electrolyte reservoirs were continuously purged with nitrogen. 10 mM TEMPTMA solution in 1 M KCl was used on the positive side and 0.5 M ZnCl₂ solution in 1 M KCl was used on the negative side. The electrolyte volume was fixed at 25 mL on both sides. For the battery test, the positive solution was electrochemically charged at + 1.10 V *vs* SHE as upper cut-off potential for 12 hours and discharged at + 0.41 V *vs* SHE for the same amount of time. The same experiment was then performed in the presence of the solid electrochemical energy storage materials, *e.g.* 100 mg of CuHCF or CNT-CuHCF composite. Once the mediated-electron transfer was demonstrated, galvanostatic cycling at 2.5 mA cm⁻² was performed in the same system over 25 cycles and within the same potential window.

2.6 Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS)

Scanning electron microscopy (FEI SEM Teneo) was performed at 1-5 kV, 0.12-1 pA with lower in-lens and in-column detectors. Different samples were imaged after drop-casting on a gold foil. The *ex-situ* composite composition was acquired by XPS. A drop of 20 µL composite or pristine MWCNT was deposited onto glassy carbon electrode and allowed to dry under vacuum. The spectra were calibrated with the C-C bound of the adventitious carbon contamination at 284.8 eV.

2.7 Ex-situ Powder X-ray diffraction (PXRD)

PXRD pattern of as-synthesized CuHCF sample was recorded by a Bruker diffractometer with Cu K_α non-monochromic irradiation ($\lambda = 1.5406 \text{ \AA}$), operated at 40 kV and 40 mA. Crystal structure with space group Fm-3m was confirmed and diffraction patterns were recorded between 10° and 90° 2θ with a step of 0.01° and 1s of acquisition time per point. Lattice

parameter ($a = 10.03 \pm 0.005 \text{ \AA}$) was determined using a Rietveld refinement in TOPAS5 package.

2.8 Computational methods

Density Functional Theory (DFT)

All calculations were done with Quantum Espresso 6.1.³⁹ The electrons were described in the formalism of the DFT+U, using projector augmented waves pseudo-potentials and the PBE-Sol exchange and correlation functional. The Hubbard parameter was set to 1 for the iron atoms and 3 for the copper atoms. An energy cut-off of 950 eV was used and a Monkhorst-Pack grid of $4 \times 4 \times 4$ k points ($12 \times 12 \times 12$ for the calculations of the electronic properties, *i.e.* density of states and conductivity). A gaussian smearing of 0.01 Ry was used in every calculation. The geometry of each structure was first optimized (cell and atoms) prior to the calculation of the electronic properties (band structure, density of state, conductivity). The electrical conductivity of the compounds was calculated using the Kubo-Greenwood formula with the help of the KGEC code.⁴⁰

COMSOL Simulation

Finite element simulations were performed on COMSOL 5.4. The model based was adapted from the example "1D Isothermal Nickel-Metal Hydride Battery",⁴¹ and modified accordingly to study the scan rate dependency of the cyclic voltammetry on the CuHCF composite electrodes, as described in the SI.

3 Results and Discussion

3.1 CuHCF characterization

Characterization of the pristine material by X-ray powder diffraction suggested a pure F-centered cubic cell with a space group of Fm-3m and a lattice parameter of 10.2 Å. Fig 1A-top represents *ex-situ* PXRD patterns of potentiostatically charged and discharged CuHCF and comparison with as-synthesized sample. All peaks were indexed within Fm-3m cell. According to diffraction selection rules, (111) reflection is prohibited for a pure F-centred cubic cell (Fm-3m for alkali-free Prussian blue analogue). However, increasing of the alkali-metal content during a discharge process led to redistribution of K^+ ions around crystallographic position, so giving rise to (111) peak. Therefore, the intensity of (111) reflection was higher for the fully discharged sample (violet curve), when all alkali sites were occupied by K^+ ions, and lower for the fully charged sample (red curve), when all K^+ were substituted by water. Influence of the state of charge on the lattice parameter (a) is plotted in Fig. 1A-bottom. Contrary to a simple linear dependence of lattice parameter (a) presented by Wessells *et al.*⁴⁷ based on calculation of a from only 400 diffraction peak, after full profile refinement, we observed such a linear dependence only after reduction of $\sim 30\%$ of Fe^{3+} . The latter is in a good agreement with recently reported $\sim 20\%$ by Svensson's group.⁴⁸

Scanning electron microscopy (SEM) pictures of the pristine and carbon-coated CuHCF materials recorded with in-lens detector are presented in Fig.2B. The pristine material showed nanoparticles with size ranging from 50-100 nm. The grape-like shape of the CB is responsible for the aggregation of the CuHCF particle as compared to the CNT in which Prussian blue analogue is well-dispersed over the surface.

Figure 1: (A) Top: Obtained PXRD patterns of as-synthesized materials as well as after charging and discharging in chronopotentiometry mode modeling real cell behavior. Peaks marked with a star were attributed to residuals of KCl. Insert: a magnified view of 220 peak. Bottom: Lattice parameter of cubic Fm-3m structure of Prussian blue (*a*) vs State of Charge. The calculated errors bars for *a* are smaller than the dots. (B) SEM picture of the CuHCF (top), CB-CuHCF (middle) and CNT-CuHCF (bottom) obtained without any conductive coating layer (in-lens detector, 1kV, 1.6 pA).

CNTs have many advantages (flexibility, high young modulus, high specific surface area)⁵⁵ and therefore are considered particularly interesting for large electronic conductivity enhancement. Due to their morphology, it enhanced non-faradaic capacitive storage⁵⁶ as already observed by Sathiya and co-workers.^{57,58} CNT pseudo-capacitance on the whole capacity was estimated to be less than 9% when the concentration of CuHCF was about 3.4 mg mL⁻¹ in the ink (Fig S9). To minimize this effect, we synthesized a composite containing 90% of CuHCF and 10% of CNT, assuming that the influence of the pseudo-capacitance (double layer capacitance) will be negligible after a short time of charge or discharge of the solid material. The final CNT-CuHCF composite was characterized by XPS (Fig S8). Pristine CNT appears without any metallic impurities of Fe, usually observed owing to their synthetic route. The composite exhibits typical binding energies of 2p orbitals for Cu and Fe and 1s orbital for N, demonstrating the successful functionalization of the CNT sidewall by CuHCF.

3.2 Investigation of K⁺-intercalation within the solid lattice of pristine and carbon-coated CuHCF: influence on the electrochemical properties

Cyclic voltammetries of pristine CuHCF, CB-CuHCF and CNT-CuHCF were performed after drop casting the inks onto a glassy carbon electrode (Fig 2A) in 1 M KCl. In all the case, the oxidation and reduction peaks are attributed to a single electron transfer mechanism for the reduction of Fe³⁺ to Fe²⁺ at a half-wave potential of + 0.950 V vs SHE, in good agreement with what was described by Engel and Grabner.³⁶ The faradaic current increased with the addition of carbon material while keeping the amount of CuHCF constant, indicating that the amount of active CuHCF increases upon addition of the carbon materials. For example, the surface concentrations of CuHCF, CB-CuHCF and CNT-CuHCF calculated based on the passed charge upon oxidation during the CV are equal to 40, 62 and 73 nmol cm⁻², respectively. Therefore, the addition of CNTs increased the amount of active CuHCF by 46% as compared to the pristine material.

Galvanostatic cycling of GC electrodes modified with CuHCF, CB-CuHCF and CNT-CuHCF was performed at different current densities in the presence of 1 M KCl (Fig. 2B). The theoretical specific capacity of CuHCF is ranging from 62 mAh g⁻¹ for the hydrated form (3.7 molecules of water in the crystal lattice) to 85 mAh g⁻¹ for the anhydrous form,⁵³ so the experimental capacities should be in similar range. CuHCF exhibits average experimental gravimetric capacity of only 2 mAh g⁻¹ at 140 μ A cm⁻² obtained after 10 cycles in 1 M KCl (Fig. S6). The latter number was calculated taking into account the whole amount of CuHCF deposited onto the electrode surface (24 μ g). Gravimetric capacities of CB-CuHCF and CNT-CuHCF were found to be 7 mAh g⁻¹ and 70 mAh g⁻¹, respectively. In this case, the deposited total mass of CuHCF was 17 μ g, based on CuHCF concentration in the ink, and the contribution of the carbon-based materials on the whole gravimetric capacity is about 4% (Fig. S7 and S8).

Figure 2: (A) Cyclic voltammetry of CuHCF (red), CB-CuHCF (30-70wt%) (blue) and CNT-CuHCF (green) in 1 M KCl at 10 mV s^{-1} , drop-casted onto glassy carbon electrode. (B) Galvanostatic cycling of pristine CuHCF, CB-CuHCF, CNT-CuHCF drop-casted onto GC electrode performed at $700 \mu\text{A cm}^{-2}$ with cut-off potentials of +0.41 and + 1.20 V vs SHE in 1 M KCl.

Such a small capacity of the CuHCF in the absence of any conductive additives is explained by the poor electronic conductivity of the material. An estimation of the active surface area from the integration of the faradaic current of oxidation on the CV gave mass of $0.96 \mu\text{g}$, meaning that only 4% of the whole deposited material is active during the CV. The percentage of active material during the CVs was estimated to be 8% in the case of the CB-CuHCF and 17% for the CNT-CuHCF. This highlights that sufficient amount of conductive additives is required to guarantee good electron transfer rate between the particles upon cycling. DFT calculations presented in the supporting information confirm the poor conductivity and the semi-metallic behavior of the CuHCF.

Scan rate dependency of the different films is presented in the SI. As already reported and observed for CuHCF and CB-CuHCF,^{36,49–51} oxidative and reductive peak currents depend linearly with the square root of the scan rate at high scan rates. This indicates that the oxidation of the CuHCF is limited by the transport of potassium in the solid particle. CNT-CuHCF films exhibit two kinetics (Fig. S3A). At low scan rates ($< 40 \text{ mV s}^{-1}$), a linear voltage dependency over peak currents was observed (Fig S3B). At higher scan rates ($40 - 100 \text{ mV s}^{-1}$), the linear dependence of the peak current over square root of the scan rate is observed, indicating a surface confined reaction (Fig S3C).

The effect of the carbon additive was investigated by finite element simulations presented in the SI. Indeed, the model can reproduce the transition from linear to square root dependence of

scan rate. At slow scan rates, the whole solid particles are reactive (in this case the response resembles that of a surface confined reaction), but at higher scan rates the potassium ion concentration in the solid particle varies significantly between the surface and the center of the particle (a radial diffusion-controlled reaction). Notably, as the rates of diffusion and electron-transfer in solid material coupled, it is not possible to evaluate them separately. However, earlier electrochemical impedance spectroscopy results showed an electron-transfer rate of $0.1 \text{ cm}^2 \text{ s}^{-1}$, meaning the rate of charge propagation in solid is limited by the movement of K^+ in a solid lattice with a rate from 10^{-10} to $10^{-9} \text{ cm}^2 \text{ s}^{-1}$.⁴⁸ Furthermore, the model shows that the slope of the peak current vs square root of the scan rate plot highly depends on the conductivity of the porous composite electrode (Fig. S5A). The secondary current distribution within the porous electrode is significantly affected by the electronic conductivity of the solid material: if the solid-phase conductivity is poor, the large ohmic drop in the electrode leads to a situation where the charge transport takes place preferably by ionic conduction in the electrolyte phase, and much of the porous electrode is inactive (Fig. 5A). In this case, the current distribution is mainly influenced by the resistance of the solid. However, if the conductivity in the porous electrode is similar or better than in the electrolyte, the current distribution is controlled by electrochemical reactivity, and the whole electrode is uniformly active (Fig 5B).

To summarize, conductive additives have two roles: they improve the connectivity between the CuHCF particles and the electrode, and they improve the secondary current distribution within the porous electrode so that the whole electrode is electrochemically active. In the absence of conductive additives only the CuHCF particles in good electrical contact close to the electrode surface undergo oxidation, while addition of CNTs enables the oxidation of almost all the CuHCF particles. In both cases, at slow scan rates the whole particles are oxidized, while at fast scan rates only the surfaces of the CuHCF particles are oxidized and the reaction is limited by the radial diffusion of the potassium within the particles.

3.3 Electrochemical charging of CuHCF and CNT-CuHCF composite using TEMPTMA as redox mediator

TEMPTMA is a TEMPO derivative substituted with a ionic trimethylammonium chloride group (Fig. 4A). Addition of the quaternary amine ensures an high solubility limit of 2.3 M in 1.5 M NaCl.²⁴ The solubility limit of the oxidized TEMPTMA²⁺ state was not reported, but based on the reversible cycling data at high concentrations it appears to be sufficiently soluble. As shown on Fig. 4B, the reversible one electron-transfer oxidation of TEMPTMA⁺ into TEMPTMA²⁺ occurs at + 0.944V *vs* SHE and is well-aligned with the redox potential of CuHCF (+ 0.950V *vs* SHE). The formal potentials are exactly matching to ensure the mediated-electron transfer in between TEMPTMA and CuHCF. This is in good agreement with the Marcus theory,^{59,60} showing that the electron transfer kinetics between two redox species are determined by the driving force, the reorganization energy and the distance between the two redox centers.

Figure 2: (A) The redox reaction for TEMPTMA and CuHCF, (B) Cyclic voltammetry of CuHCF drop-casted onto GC electrode in 1 M KCl (grey, in mA g⁻¹) and 10 mM TEMPTMA (blue, in mA·cm⁻²) on a bare GC electrode as working electrode. (10mV s⁻¹). (C) Cyclic voltammetry of CNT-CuHCF in 1M KCl (black, in mA·g⁻¹), 10 mM TEMPTMA (red, in mA·cm⁻²) on CNT and CNT-CuHCF in 10mM TEMPTMA (blue, in mA·g⁻¹) drop-casted onto GC electrode at 10 mV s⁻¹.

Fig. 4C shows the cyclic voltammetry for a modified CNT-CuHCF electrode in the absence and presence of TEMPTMA. 3-fold enhancement of the maximum oxidative and reductive peak current is in good agreement with a mediated-electron transfer in between the TEMPTMA and the Prussian blue analogue. In fact, the residual maximum peak current is smaller for a simple CNT electrode. Same trends were observed without (Fig. S12) and with carbon black (Fig S13). Peak-to-peak separation for the oxidation of 10 mM TEMPTMA in 1 M KCl in the absence of CuHCF on planar GC electrode is ca. 60 mV, but increases to 140 mV on CNT electrodes, indicating actually lower activity of CNTs for the electrochemical oxidation of TEMPTMA. However, this evaluation is complicated by the porous structure of the CNTs, as highlighted by by Streeter *et al.*⁶¹

Cyclic voltammetry of the composite electrodes in the presence of TEMPTMA was performed at different scan rates (5-100 mV s⁻¹). Two distinct kinetics were observed for CB-CuHCF (Fig. S15) and CNT-CuHCF (Fig. S16) ranging from a surface confined at low scan rate to a

diffusion-limited process at high scan rates. Decreasing of peak-to-peak separation and increased peak currents in the presence of TEMPTMA for the Prussian blue analogue-modified electrode suggest a faster heterogeneous electron transfer coming from the mediation in between the CuHCF and the TEMPTMA. Therefore, TEMPTMA-mediated electron transfer has a “catalytic effect” on the electron transfer.

Fig 5 shows the equilibration of the Fermi levels between the flow battery electrode, TEMPTMA, CNT and CuHCF. This illustration is useful to show the thermodynamics of the system, and represents simply the equilibration of the electrochemical potentials of the electrons through electron transfer reactions, as recently illustrated.^{62–64} As TEMPTMA is constantly recirculated through the flow battery cell, its redox potential is considered to be in equilibrium with the electrode. Upon contact with the CNT-CuHCF composite, the Fermi levels between solid and TEMPTMA species equilibrate. If the Fermi level of electrons in the TEMPTMA species is higher than the Fermi level of the composite, TEMPTMA will reduce the CNT and CuHCF until equilibrium is reached (Fig. 5A). In the case where the Fermi level of the CNT-CuHCF composite is initially higher than the Fermi level of electrons in TEMPTMA in solution, electrons will transfer to the TEMPTMA species until equilibrium is reached (Fig. 5B). For CuHCF, the equilibrium of the Fermi level requires modification of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio as well as the accompanying intercalation/deintercalation of K^+ , while electrostatic charging accompanied by the modification of the electric double layer is required to shift the Fermi level of the CNTs. The equilibrium between 50% state-of-charge (SOC) electrolyte and the CuHCF is reached when SOC of the CuHCF reaches 17 %, as calculated from state of charge data from ref. 35. 99% SOC electrolyte equilibrates with SOC of 86 % of the CuHCF, indicating that TEMPTMA mediated electron transfer can be utilized to access ca. 80% of the capacity of the CuHCF. However, the SOC data in ref. 35 is obtained in different electrolyte. Furthermore, the voltammetry in Fig. 4B shows an excellent match between the formal potentials of TEMPTMA and CuHCF, indicating that even higher percentage of the capacity of the solid material can be accessible.

Figure 5: (A) Fermi level equilibration of CNT-CuHCF composite with TEMPTMA species in solution, when oxidation state of TEMPTMA is fixed by the flow battery electrode, at state of charge of 50% and 99% (B). The state of charge data for CuHCF is taken from ref. 35. Potentials are converted to Fermi levels by taking the Fermi level of SHE as -4.44 eV. (Note that the Gerischer-Marcus representation⁶⁵ of the solution states of the TEMPTMA has been shifted to allow sufficient scale for the potential variation. In correct presentation, the energy levels of the maximums for the state density distributions of solution states should be constant.)

Galvanostatic cycling ($+ 1.10$ V *vs* SHE and $+ 0.40$ V *vs* SHE) tests were carried about to study the electrochemical charge/ discharge of the solid material via the redox mediator and the consequent capacity enhancement. Three different systems were studied as follow: 1) 10 mM TEMPTMA electrolyte (in 1 M KCl), 2) 10 mM TEMPTMA along with 100 mg of CuHCF solid material and 3) 10 mM TEMPTMA with 100 mg CNT-CuHCF (composite) solid material (Fig 6).

Figure 6: (A) Charge capacity and (B) discharge capacity obtained for 10 mM TEMPTMA without solid material (black line) and with 100 mg CuHCF (dashed blue line), and 100mg composite (red line) performed at +1.10 V vs SHE and + 0.41 V vs SHE using 25 mL of 1 M KCl solution, under nitrogen purging.

In the case of the redox mediator alone (TEMPTMA, black line in Fig. 6A), a charge capacity equal to 27 C was obtained during the oxidation reaction and a discharge capacity of -24 C during the reduction reaction. The discharge capacity matches the expected theoretical capacity of 24 C, but 1.125 times higher charge capacity indicate that some side reactions such as oxygen evolution are taking place.

In the presence of 100 mg of CuHCF powder and 10 mM TEMPTMA, apparent charge and discharge of 45 C were obtained, corresponding to an efficiency of 96% according to the theoretical charge (47 C). The latter is the sum of the theoretical charge of TEMPTMA and the theoretical charge for 100 mg of CuHCF (*e.g.* 23 C, calculated with the theoretical capacity of 62 mAh g⁻¹). Utilization rate is lower if the anhydrous capacity (85 mAh g⁻¹) is used instead.

Finally, the CNT-CuHCF composite was tested in the same condition, charge and discharge capacities of 59 and 60 C were obtained, respectively. The gravimetric capacity of the composite seems to be closer to the one of the anhydrous CuHCF form (85 mAh g⁻¹). Hence, the theoretical charge of the composite in the presence of TEMPTMA was found to be 51 C (*e.g.* 27 C for the CNT-CuHCF and 24C for 10 mM TEMPTMA). Again, the apparent charge is 1.17 times higher than the theoretical value. This cannot be due to side reactions such as oxygen evolution, as the capacity is reversible, but could be due to the pseudo-capacitive

properties of the carbon nanotubes or to the π -stacking of TEMPTMA on the CNT sidewall, leading to inner surface side reactions.⁶⁶ These experiments demonstrate that almost all the capacity of the solid material can be accessed with TEMPTMA electrolyte.

To demonstrate the ability of these solid energy storage materials to enhance the storage capacity of the whole electrolyte, these results were compared in terms of volumetric capacities. Therefore, apparent gravimetric densities for CuHCF and the composite were found to be 1.33 (± 0.1) g mL⁻¹ and 1.41 (± 0.1) g mL⁻¹. This corresponds of a volume of storage solid material of 0.075 mL for CuHCF and 0.071 mL for the composite within 25 mL TEMPTMA electrolyte solution. Table 3 summarizes experimental volumetric capacities obtained as aforementioned together with the respective theoretical values.

Table 3: Summary of the theoretical volumetric capacity and apparent volumetric discharge capacity of each material. The contribution of the solid material itself was calculated by subtraction of the apparent discharge capacity of TEMPTMA (-27C) to the one obtained for each solid material divided by the added volume, e.g. 0.075 mL for the CuHCF and 0.071 mL for the composite

Materials	Theoretical volumetric discharge capacity (C mL⁻¹)	Apparent volumetric discharge capacity (C mL⁻¹)
10 mM TEMPTMA	0.972	1.08
100 mg CuHCF+10mM TEMPTMA	460	240
100 mg composite + 10 mM TEMPTMA	438	464
2 M TEMPTMA	194	-
100 mg composite	437	-

CuHCF achieved only 52% of efficiency as compared to the theoretical volumetric capacity (if the anhydrous capacity of 85 mAh g⁻¹ is used) indicating that the pristine material is only partially active. In the case of the composite, the apparent volumetric discharge capacity showed an excess of 6% as compared to the theoretical value. Once again, the highest electronic

conductivity and specific surface area of MWCNT ensured the achievement of a high volumetric capacity as compared to the pristine material. The immobilization of CuHCF particles on the nanotubes prevents aggregation, favors high electron transfer rates, leading to good cycling stability and capacity retention.

Indeed, the 400-fold enhancement capacity with the composite demonstrates the ability of our system to increase the performance of our solid-aqueous electrolyte, as compared to the TEMPTMA alone. However, it is worth to mention that this enhancement needs to take into account that the concentration of TEMPTMA is very low (10 mM in 1M KCl). The specific capacity of 2 M TEMPTMA is 194 C mL^{-1} . A system with 50 v-% solid material and 50 v-% of 2 M TEMPTMA would have a volumetric capacity of 316 C mL^{-1} , a 62 % increase in comparison with the TEMPTMA solution alone. For a 90 v-% solid material the capacity would be 413 C mL^{-1} , more than doubling the energy storage capacity. The actual percentage of solid that can be introduced into the system needs to be investigated, and depends on the design of the flow circulation.

3.4 Solid electrochemical energy storage material for CNT-CuHCF-TEMPTMA /Zn aqueous redox flow battery.

An aqueous redox flow battery composed of 10 mM TEMPTMA and 100 mg composite in the positive electrolyte and 0.5 M zinc chloride in the negative electrolyte was assembled. During the discharge of the battery, the oxidation of TEMPTMA⁺ into TEMPTMA²⁺ at the RVC electrode surface is balanced with the oxidation of the solid energy storage material from Fe²⁺ to Fe³⁺, leading to the de-intercalation of K⁺ inside the composite. TEMPTMA⁺ is then recycled to TEMPTMA²⁺ at the solid-liquid interface, thanks to the driving force existing in between the composite and the redox mediator. At the negative side, Zn (II) is reduced to Zn. In the absence of solid materials, a coulombic efficiency of only 70% was obtained, mainly due to cross-over through the glass frit. The addition of composite increases the coulombic efficiency up to 95%, because the kinetics of charge transfer is faster in this case and TEMPTMA is recycled at the CNT- CuHCF interface (Fig. 7A). Galvanostatic cycling was performed at 2.5 mA cm⁻² and a discharge volumetric capacity of 350 C mL⁻¹ was obtained after 25 cycles. The composite was cycled safely over time, showing high Coulombic efficiency (almost approaching 100%) over 25 cycles (Fig. 7B). The cycling of the organic positive electrolyte solution alone is reported in the SI in Fig.S17.

Figure 7: (A) Coulombic efficiency of TEMPTMA in the absence (black dots) and in the presence of composite (black square) as a function of the number of cycles. The volumetric capacity of TEMPTMA in presence of composite over number of cycle is plotted along the secondary y-axis (red dots). B) Positive electrolyte potential as a function of time. Cycling parameters: galvanostatic mode at 2.5 mA·cm⁻² with charge and discharge cut-off potentials equal to + 1.10 and

+ 0.60V vs SHE, respectively. The cycling test was performed over 25 cycles in the presence of 100 mg composite and 10 mM TEMPTMA in 1 M KCl at the positive side and 0.5 M ZnCl₂ in 1M KCl at the negative side.

However, 25% of capacity fading (as compared to the theoretical volumetric capacity of 460 C mL⁻¹) was observed. Overall, a 10⁴-fold increase of capacity was achieved with the addition of CNT-CuHCF composite at the positive side electrolyte of the system. Such enhancement in the storage capacity makes this candidate couple promising for large-scale flow battery installations.

A simplified cost estimation was done for the system 4-Hydroxy-TEMPO (TEMPOL) / CuHCF. TEMPOL was chosen as electrolyte material because it is commercially available instead of TEMPTMA as electrolyte material. All the prices of the chemicals were obtained from Alibaba.com (accessed 04 March 2019). The costs were calculated assuming all reagents to be purchased on ton quantities. The prices used are the follows: 4-Hydroxy-TEMPO (4.4 €/kg) and p-CuHCF (calculated simply as addition of copper sulfate and potassium ferricyanide) (1.3 €/kg and 1.1 €/kg). Based on these prices, the material costs to synthesize 1 kg of CuHCF is 2.8 €/kg. Then, assuming a final redox flow battery with a nominal cell voltage of 1.5 V and considering the specific capacity of 62 mAh/g the energy cost of CuHCF would be 30 €/kWh. The cost of TEMPOL would be 110 €/kWh, highlighting that utilization of boosters from inexpensive raw materials can decrease the RFB system cost significantly. For example, a system with 90 w-% of CuHCF and 10 w-% of TEMPOL would have a cost of 33.5 €/kWh. If materials of similar cost and capacity would be used for the negative side, the cost of the chemicals of such a RFB system would be 67 €/kWh. Considering the high current chemical cost and the price volatility for the vanadium flow battery (800 €/kWh in the end of 2018 to 200 €/kWh in the summer of 2019, calculated as in ref. 67, changing only the cost of vanadium as given in <https://www.vanadiumprice.com/> for vanadium only), this low cost shows that a similar system should be feasible. Note that this simplified cost estimation considers only the cost of the chemical, excluding the cell stacks, tanks, ancillary equipment, etc., as well as synthesis costs.

4 Conclusions

A solid electrochemical storage strategy was developed for RFBs operating with a TEMPO derivative and Prussian blue analogue. The addition of less than 10% CNT to the CuHCF Prussian blue material promotes the charge transfer and leads to a gravimetric capacity of *ca.* 70 mAh g⁻¹. The redox potentials of TEMPTMA and CuHCF of +0.944 and +0.950 V *vs* SHE in 1 M KCl are close enough to mediate the electron transfer at the solid-liquid interface.

Finally, cycling behavior of CuHCF-TEMPTMA/Zn aqueous redox flow battery was investigated. An excellent coulombic efficiency up to 95% was achieved after 25 cycles. Furthermore, a significant increase of the volumetric capacity was obtained in the presence of 100 mg of composite in the positive electrolyte, highlighting for the first time the excellent booster capacity of the Prussian blue analogue. Hence, redox solid-boosters are promising candidates as inexpensive materials to increase the energy density of organic aqueous RFBs.

5 Acknowledgements

The authors would like to thank Dr. Emad Oveisi for his advice on scanning electron microscopy. The authors acknowledge financial support from EOS Holding SA. This work was performed within the Swiss Competence Center for Energy Research (SCCER) Heat and Energy Storage (HaE) framework. P.P. gratefully acknowledges the Swiss National Science Foundation for an Ambizione Energy grant (160553), and the Academy Research Fellow funding from the Academy of Finland (Grant number 315739).

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