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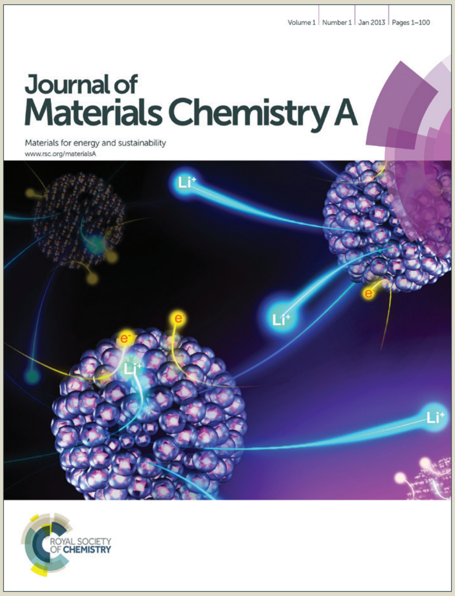

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Metal Organic Complexes as Redox Candidates for Carbon Based Pseudo Capacitors

Arie Borenstein[a], Ohad Fleker[a], Shalom Luski[a], Laurent Benisvy[a] and Doron Aurbach[a]*

a Chemistry Department, Bar-Ilan University, Ramat Gan, 5290002 Israel.

*Tel:972-3-5318317
Fax:972-3-738-4053
Email: aurbach@biu.ac.il

Webpage: http://www.ch.biu.ac.il/people/aurbach

1. Introduction

Super capacitors (SC) are energy storage devices that have gained in interest in recent years. Storing energy via electric double-layer capacity (EDLC) interactions enables SCs to possess very high power density and nearly unlimited cyclability. However, since EDLC involves only weak electrostatic interactions, SCs are inferior by orders of magnitudes to batteries in terms of energy density . [1-4] Activated carbons (AC) are the common material for electrodes for SC systems. ACs are well-known for their potential for extremely high surface area and remarkable ability to bind a wide variety of molecules. Pseudo capacitors (PSC) achieve greater energy density than SCs by adding redox active materials to the surface of the electrodes. PSC can store energy by two parallel routes: EDLC on the carbonaceous electrodes and faradaic reactions of the redox moieties, yet, no chemical reactions involving changes of the molecular components occur, what enables a very fast charge transfer and stability upon long cycling. [5-8] Two groups of materials are often used as PSC redox species: metal oxides and conducting polymers. Unfortunately, both suffer major drawbacks such as electrical conductivity issues in at least one of their redox states and fast degradation on cycling. There are reports in the literature on attaching redox-active moieties to carbonaceous electrodes in order to enhance their specific capacity. However, in many cases such systems suffer from weak linkages between the redox moieties and the carbonaceous electrodes , what leads to a loss of contact (and hence effective electrochemical activity) upon cycling . [9-11]

In this study, we present a new type of redox active material for PSC, namely, metal-organic complexes (MOCs), which have the potential to overcome the current PSC limitations as they have good conductivity and also bond strongly to activated carbon (AC) surfaces. Due to their aromatic framework, MOCs allow reasonable electrical contact and a facile flow of electrons via π-π bonds with graphitic-like sites that are usually present in all types of amorphous carbons. [12-14] MOCs were combined with the AC electrode surfaces using two different methods, each with its own advantages: wet physical adsorption in solutions and adsorption from the gas phase. Some studies involving redox-active MOC for different purposes were already carried out [15-16], however the present study is a first attempt to benefit from the aromatic ligands of the red-ox moieties to facilitate their strong adsorption to the carbonaceous electrodes.

Here we present a novel approach and results related to simple complexes adsorbed on AC electrodes for PSCs. The MOCs considered comprise a wide variety of ligands and metals, leading to interesting optimization possibilities. We present results related to both aqueous and non-aqueous systems. For both types of electrolyte solutions , the mechanism of charge storage involves both fully capacitive interactions in and red-ox interactions, in which the oxidation state of the iron ions changes. In both types of interactions, the electrode charging-discharging processes are compensated by counter-ions adsorption and desorption.

2. Experimental

2.1 Materials

Ferrocene, Phenanthroline and bipyridine compounds used in this study were purchased from Sigma-Aldrich. Ferroin (Fe(phenanthroline)$_3$) and iron tris-bipyridine (Fe(bipyridine)3) were papered by mixing methanolic solutions of ferrous perchlorate and the organic ligands. The resulting solutions were filtered through cotton. Crystals were grown in -18 ^{0}C for ca. 2 weeks. The crystals were filtered and washed with diethyl ether. The ferroin activated carbon fibres (ACF, Kynol 1500) were obtained from Kynol Inc. (USA) and the activated carbon powder from Midwestvaco (USA, ~2100 m^2/g). Porous poly-ethylene (PE) separators from Tonen Chemical Corp were used. The electrolyte solutions containing 1.4 M tetra-ethyl-ammonium tetra-fluoroborate (TEA-BF$_4$) in acetonitrile (AN), were purchased from Honeywell and polyvinylidene fluoride polymer (PVDF) from Kynar, Arkema. The carbon black used in this study was super P carbon from Timcal, Switzerland.

2.2 Electrode preparation

Attaching MOC to the activated carbon electrode surfaces was carried out by several methods. Fc /activated carbon fibers (ACF) electrodes were prepared by mixing Fc/ACF (1/1, w/w) in AN under mild heat (70 ^{0}C) until complete physical adsorption was achieved. Then the solvent was evaporated and the mixture was dried and the composited powder was mixed with PVDF binder (10%) and carbon black (5%). The slurry was pasted on aluminum foil current collectors and the resulting composite electrodes were dried in vacuum overnight. The electrodes were cut into 11 mm diameter discs and their active mass weight was around 5 mg. In a parallel electrode preparation method (via adsorption from the gas phase) activated carbon fiber (ACF) felts (11 mm diameter, 9 mg active mass) were placed in vials with a pre-measured amount of Fc. The vials were vacuumed and heated to 150 °C for 10 hours until completed impregnation of the complex into the ACF electrodes was obtained (the full sublimation of the MOC was visually confirmed and it was clear that all of it was adsorbed by the carbon). In the wet adsorption method, 4 mM of the MOC in AN were introduced into a vial containing the activated carbon fibre sample. This mixture was left at room temperature until complete physisorption was achieved.

2.3 Instruments

All the electrochemical measurements were carried out with potentiostate/ galvanostate computerized instruments from Bio-Logic Inc. Computerized multi-channel battery analyzers from Arbin Inc. were used for prolonged cycling measurements (voltage *vs.* time at constant currents). The quasi-reference electrode used in this study was Platinum wire (Sigma Aldrich), after determining its stability compared to the standard Ag/AgCl reference electrode (Bio-Logics, France). The gas adsorption properties of the san Autosorb-1 MP (Quantachrome, Florida USA) system. The specific surface area was calculated using the BET model. SEM images were obtained by FEI Inspec S (FEI Company, USA). Uv-vis spectra were measured using Cary 5000 UV-vis-NIR spectrophotometer (Agilent, California, USA). Thermal gravimetric analysis (TGA) was carried out in TGA/DSCI 1 analyzer (Mettler-Toledo, OH, USA). Inductively coupled plasma- atomic emission spectroscopy (ICP-AE) was measured using Ultima 2 (Horiba Scientific, Japan).

3. Result and discussion

3.1 Electrodes prepared with an active mass obtained by physical adsorption of dissolved Ferrocene (Fc) onto AC powder.

The Fc/Fc+ redox couple was chosen due to its frequent use in inorganic electrochemistry, and its good reversibility. Fc dissolves in many organic solvents but is only negligible soluble in water (7.68×10^{-7} mole fraction) . [17] For this reason, we adopted the following method: we loaded Fc on the electrodes in an organic medium, but measured the electrodes in aqueous solution, in which desorption of Fc from the electrodes during electrochemical operation is fully avoided. The electrolyte solution chosen was aqueous 1 M Li_2SO_4 that enables a relatively wide electrochemical window (for aqueous solutions). [18-19] The CV measurements of cells consisting of a composite activated carbon fiber (ACF) electrode as working electrode, ACF (higher weight) as a counter electrode and platinum wire as pseudo reference electrodes, are presented in Fig. 1a. The reliability of using Pt wires as very stable pseudo-reference electrodes function as pseudo reference electrode was tested and approved in specific long term experiments vs. standard calomel electrodes. Once we proved it, it was most convenient to use thin Pt wires as reference electrodes in the experiments reported herein. The redox potential of these electrodes is similar to that of unbound Fc in solution (-0.17 V vs Pt, marked in Fig. 1a). The specific capacitance of the anodes in the cells ($-0.26 < V < 0.32$, within which the redox reaction occurs) is 160 F per gram of active material (AC+Fc). For comparison, a CV profile of an AC electrode exhibiting only 85 F/g is also presented. We then closed two-electrode coin-cells with AC counter electrode weight-balanced according to the previous results. In galvanostatic charge-discharge measurements (constant current density of 100 mA/g) the capacitance obtained from the working electrode was 143 F per g of the active materials (Fig. 2b). This result is in excellent agreement with the capacitance obtained in CV measurements of this cell (Fig. 2c). CV measurements at different scan rates were conducted. Due to Fc's fast redox reaction, the specific capacitance of the electrodes declines only moderately at fast scan rates demonstrating a retention of about 80% when the scan rates are 10 times higher (see Fig. 1a). Cycling these aqueous cells at 1mV/s reveals reasonable capacity retention during thousands of cycles (Fig. 1c). These results demonstrate that using MOCs as active redox moieties for pseudo capacitors may be a promising practical approach.

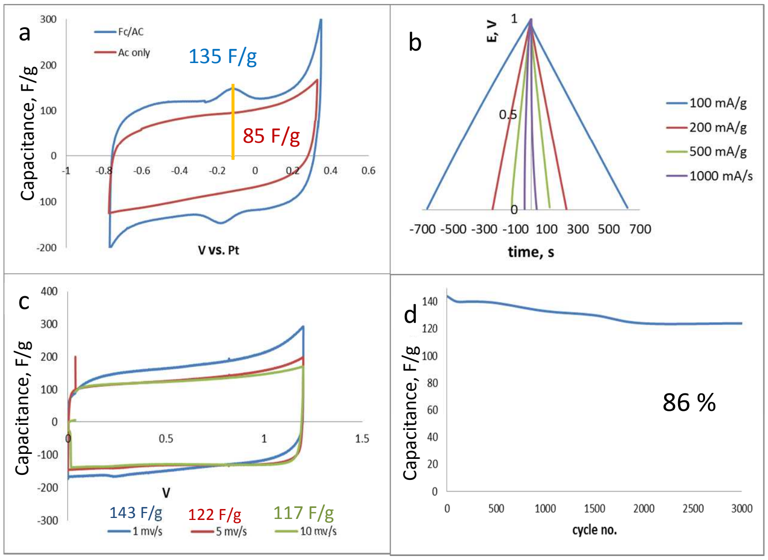

Fig. 1: a. Studies in three-electrode cells of Fc/AC powder 1:1 (w/w) composite electrode, with Pt wire quasi-reference electrode in aqueous 1 M Li_2SO_4. A typical steady state CV measured at 1 mV/s is presented (the blue line). The red curve relates to AC powder electrodes without Fc. The oxidation potential of unbound Fc in the same solution is marked with a yellow line. b. Typical steady-state galvanostatic cycling with potential limitation of weight-balanced two-electrodes coin-cells at 100, 200 and 500 mA/g ("negative" time denotes for time before discharge). c. CVs of the same system as b at 1, 5 and 10 mv/s, the specific capacitance of each scan rate is marked in. d. Prolonged galvanostatic cycling behavior of the two-electrode cells at 100 mA/g.

3.2 Electrodes prepared with an active mass obtained by adsorption of Fc into activated carbon fibers (ACF) from the gas phase.

Another useful method for elaborating Fc/ACF composite electrodes is by vapour adsorption (the standard boiling point of Fc ~180℃, which is of course much lower at reduced pressure). It was recently reported that the highly porous structure of ACFs may allow a large mass loading of active materials for pseudo-capacitive electrodes with homogeneous dispersion, and that they can easily be stacked together without loss of performance. [21] In order to optimize the carbon/MOC ratios of the composite electrodes, electrodes with Fc loading of 25%, 20%, 16.6%, 12.5%, 10% (Fc/AC wt%) were prepared. The Fcs can be nicely seen in scanning electron microscope (SEM) image (Fig. 2a) where they appear in the pores of the electrode indicating their effective impregnation into the carbon matrix (Fig. 2a). Elemental analysis by energy dispersive x-ray (EDAX) spectrometry performed on electrodes containing 16.6% Fc indicates the presence of gravimetric 6.6% iron atoms (Fig. 2b). Taking into account that iron constitutes about a third of the weight of the complex, the EDAX results confirm the predicted adsorption of Fc into the carbon electrode. Thermogravimetric analysis (TGA) measurements comparing unbound Ferrocene with a composite electrode containing 10% Fc is presented in Fig 2c. While the unbound Fc was completely evaporated at 150°C, the adsorbed Fc vaporization continues up to 300°C. This indicates the strong bonding of the complex to the carbon surface.

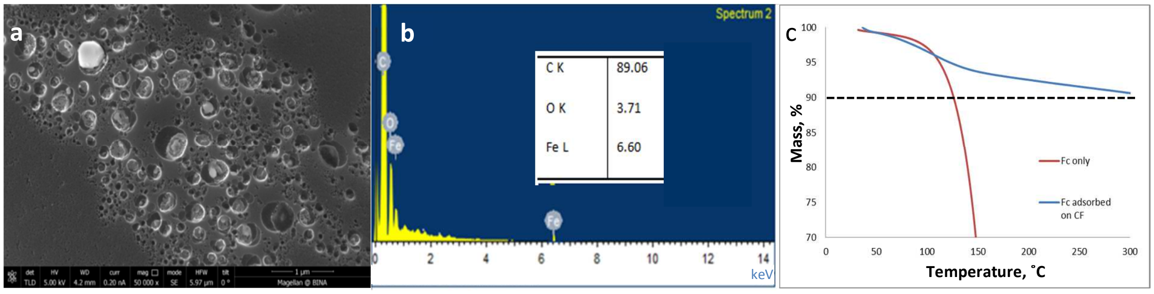

Fig. 2: a. SEM image of Fc impregnated into pores of activated carbon fibers containing 16.6% Fc (w). b. EDAX data related to the image presented in Fig. 2a, and a table presenting the weight distribution of carbon, oxygen and iron atoms. c. TGA results for Ferrocene (red) and a composite electrode containing 10% Fc (blue). The gravimetric division of the complex is marked by a black dashed line.

The results of gas adsorption measurements of composite electrodes with different Fc loading are presented in Fig. 3a and Table 1 (average values of 3-4 measurements for each loading ratio is presented). It is clear that the Fc diffuses into the carbon matrix and blocks some of the micropores of the carbon. It is therefore reasonable to assume that the Fc molecules are not adsorbed on the carbon surface in the form of monolayer coverage, but rather form some clusters and nano-crystals. These aggregates are seen in the E-SEM image. Hence, we anticipate that not all the Fc bound to the carbon is fully electroactive in the redox reaction. Furthermore, the specific surface area (SSA) of the composite electrodes decreases as a function of the amount of Fc adsorbed, which means a decrease in the electrode surface available for EDL interactions. On the other hand, a high concentration of Fc in the carbonaceous matrix is essential for achieving high specific capacitance due to its redox reaction. There is thus a trade-off between EDLC and faradaic capacitances as a function of the level of Fc adsorption so that optimization of the Fc/carbon ratio is required. Fig. 3c presents the influence of the Fc/carbon weight ratio on the electrode SSA and its specific capacitance. The highest specific capacitance was obtained with electrodes containing 16.6% Fc by weight (145 F per g of total active mass). It is possible to calculate the theoretical faradaic capacitance according to 1 electron per molecule. By adding the EDLC contribution to the experimental SSA of each electrode, one can evaluate the theoretical specific capacitance of the composite electrodes. Comparing the theoretical value to the experimental results gives us the efficiency of the contribution of the Fc redox reaction to the electrode's specific capacity, meaning the molar fraction of the Fc adsorbed to the carbon that undergoes redox reaction. Experimental data and calculations are summarized in Table 1. Another important conclusion is that impregnating Fc into the carbon matrices from the gas phase favours forming a smooth coating, rather than the micro-size bundles formed by wet physisorption as described in the previous paragraph. We may explain it by considering that adsorption of Fc from the gas phase enables a better separation of the molecules, thus avoiding massive formation of Fc clusters on the carbon surface. The thin and uniform Fc coating facilitates more effective electrochemical reactions. This explains the fact that there is an optimal Fc/carbon weight ratio (i.e. electrodes containing less active redox material demonstrate higher specific capacitance). The galvanostatic charge-discharge voltage profile of these electrodes is presented in Fig. 3b and is compared to that of bare ACF electrodes. Two- electrode coin-cells containing composite electrodes with 16.6% Fc as working electrode and weight-balanced AC were galvanostatically cycled more than 12,000 cycles (cycling was manually stopped, not due to capacity fading) demonstrating impressive stability with only 6% capacitance fading and columbic efficiency of > 99% (Fig. 3d). After thousands of cycles, the cells were opened and the electrolyte solution was subjected to inductively coupled plasma – atomic emission (ICP-AE) measurements in order to evaluate the amount of Ferrocene that was dissolved out of the electrodes. Only 0.0069 mg of iron was found, corresponding to less than 0.5% of the iron that was loaded on the electrodes. These measurements of solution phase after prolonged cycling, showing a negligible level of the red-ox moieties in solution are in line with the prolonged cycling data , confirming that the red-ox species are bound very well to the composite carbon matrices. They do not desorb from the electrodes during prolonged cycling.

Table 1:

percent Fc of total mass electrode (%)	Theoretical Fc contribution[a] (F/g)	SSA, BET model (m^2/g)	Theoretical total capacity[b] (EDLC+redox, F/g)	Experimental capacitance[c] (F/g)	practical contribution of Fc[d] (F/g)	Fc efficiency[e] (%)
0	-	1500	85	85	0	-
25	125	730	166	115	74	27
20	100	920	180	121	69	40
16.6	83	1070	162	145	84	79
12.5	62.5	1130	140	113	49	56
10	50	1210	126	102	33	51

a- (Fc gravimetric capacity (516 F/g)) * Fc percentage

b- Theoretical + EDLC of SSA.

c- From cyclic voltammetry, 10 mV/s, 85 F/g- experimental capacitance

d- Experimental capacitance – EDLC of SSA

e- Practical contribution/ theoretical contribution

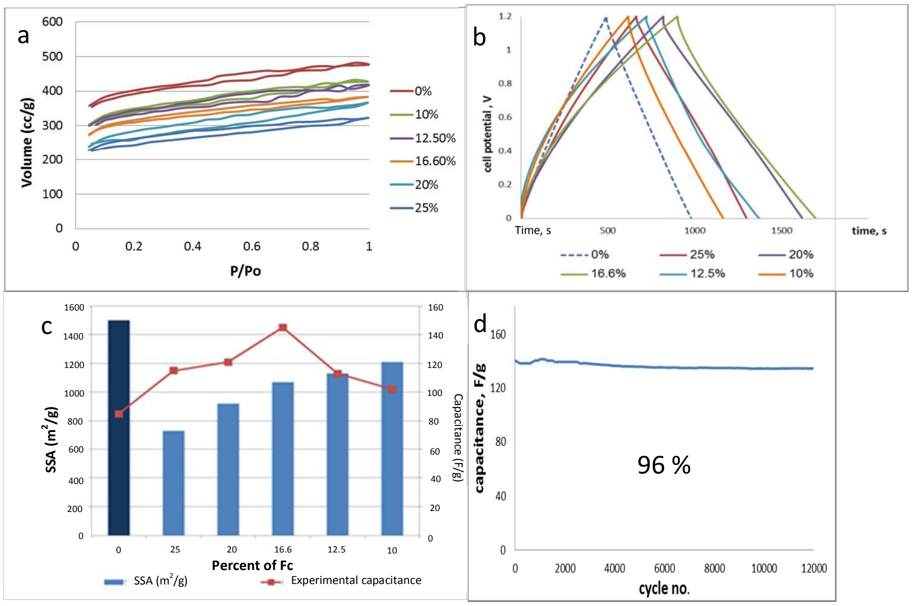

Fig. 3. a. Gas adsorption isotherms of the composite electrodes with different loadings of Fc (see legend) compared to bare activated carbon fiber (red). b. Galvanostatic charge-discharge behaviour of electrodes with different mass loading of Fc (i.e. different Fc/ACF mass ratios). 1M Li_2SO_4 aqueous electrolyte solution. Current density =100 mA/g. Results for bare ACF electrodes are represented by dashed lines. c. Specific surface area and gravimetric capacitance of composite electrodes with different Fc loading. The capacitance was calculated according to data presented in Fig. 3b, discharge between 0 to 1 V. d. Capacitance stability during prolong cycling of cells containing 16.6% Fc by weight. The specific capacitance was calculated in the same manner as in Fig. 3c.

3.3 Ferroin/ACF composite electrodes

Ferrocene demonstrated significant compatibility as a redox compound for pseudo capacitors based on activated carbon electrodes. However, Fc undergoes only one electron reaction. The basic equation for the energy density for a super-capacitor is : $E=0.25CV^2$,(V being the voltage applied, C being the electrodes specific capacity). Hence, in order to develop a SC or PSC with a relatively high energy density (relevant to the energy density scale of these devices) it is important to use redox moieties whose reaction involves more than one-electron transfer and occurs at as high potentials as possible (within the window of stability of the electrolyte solutions and the other electrode components). Consequently, we examined in this work iron complexes whose redox reactions involve multiple electron transfer and higher voltages. Another important desirable property of redox moieties for PSC that can undergo multiple electron transfer may be the large voltage span of their redox reactions so they can be used in both the negative and positive electrodes. Ferroin ($[Fe(phenanthroline)_3]^{+2}$) and iron tris-bipyridine ($[Fe(bipyridine)_3]^{+2}$) chlorides were found to fit all of these requirements. In addition to the high oxidation potential of the iron ion in these complexes, the ligands can also undergo electrochemical reactions and their reduction forms stable multi-radical production [20] Another benefit using such redox moieties is their large aromatic ligands which can bond strongly to graphitic-like clusters which are dispersed at relatively high concentration in amorphous carbons.

We have developed a special approach for determining the rate of adsorption of MOCs on ACF matrices from aqueous solutions using uv-vis spectroscopy. As the adsorption of MOC such as Ferroin and iron tris-bipyridine (ITB) chloride moieties from the solution phase into the carbon electrodes progresses, their uv-vis response at 511 nm and 524 nm, respectively, in the mother solution decreases. Hence, the magnitude of uv-vis absorption spectra of the solutions from which these MOC are adsorbed onto ACF electrodes vs. time indicates the kinetics of the adsorption process. The specific wavelengths for the spectral measurements (from which the adsorption kinetics was followed) were chosen according to the uv-vis spectra of the two MOCs , presented in Fig. 4c (in good agreement with the literature [22]). Fig. 4d shows spectroscopic results from these adsorption experiments. The rate of adsorption increases with the number of aromatic rings of the organic ligands of the MOC moiety. Accordingly, the adsorption rate of the Ferroin MOC to the activated carbon matrices was 1.52 time higher than that of the ITB MOC (Fig. 4b). The typical Langmuir shape of the adsorption isotherm, showing initially a very high rate of adsorption that then levels off, suggests that these aromatic MOCs undergo a relatively simple adsorption processes, forming mono-layers. Similar spectroscopic measurements of aqueous solutions containing composite ACF- MOC electrodes, demonstrated no release of MOC from the electrodes to the solution phase, implying that the adsorption process is almost irreversible. Once the composite electrodes are formed, they remain stable in solution.

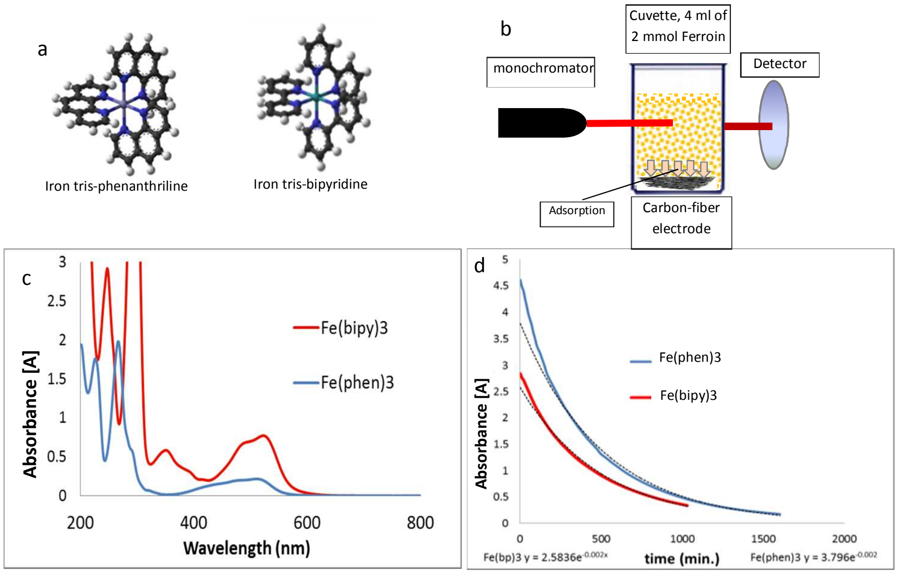

Fig. 4. a. Structural formulae of iron tris- phenanthroline (Ferroin) and iron tris-bipyridine cations. The anions used here were Cl^{-}. b. The layout of the adsorption-spectroscopic measurements. c. Typical uv-vis spectra of Ferroin-MOC and ITB-MOC in aqueous solution. d. Uv-Vis absorption vs. time of solutions containing Ferroin-MOC and ITP-MOC (responses at 511 nm and 524 nm, respectively), measured during their adsorption into ACF. The aqueous solutions contained 2 mM of MOC , adsorbed to 10 mg carbon fiber (1500 m^2/g).

In the wet physisorption process, Ferroin chloride salt was dissolved in water and the solution was put in a vial containing porous carbon fiber (1500 m^2/g). We allowed the carbon electrode to adsorb the complex during 12 hours at 100℃ until completion of the adsorption process (the solution uv-vis absorption spectra reached steady low intensity values). Typically, we managed to load about 0.004 mmol of Ferroin on each carbon electrode corresponding to 20% of the composite electrode mass.

Ferroin ions can undergo four reversible redox reactions within the electrochemical window of non-aqueous solutions based on acetonitrile (AN/TEA-BF_4)): one-electron oxidation reaction at 0.66 V vs. platinum wire pseudo reference electrode related to the iron ion and three-electron reduction reactions of the three phenanthroline ligands forming radical moieties at: -1.08, -1.85 and -2.42 V vs. platinum pseudo reference electrode

(Fig. 5a). The theoretical capacitance for the anodic reaction (one-electron transfer per molecule, related to the redox activity of the iron cations) is 175 F per g of the active materials (AC+Ferroin) and for the cathodic reaction (three- electron transfer) it is 525 F/g. Fig. 5a shows typical steady-state CV response for Ferroin-chloride/ACF composite electrodes in AN/TEA-BF_4 solutions along with a CV of Ferroin-perchlorate dissolved in the same solution, for comparison. The peak of iron ion oxidation is clearly observed. The peaks related to the reduction of the three aromatic ligands are not distinctive in the CV curves, probably due the nature of the redox reactions of the adsorbed species and the overlapping capacitive EDLC current of the carbonaceous matrix. It should be noted that the composite electrodes' capacitance has two sources: the EDLC of the carbon electrodes and the faradaic activity of the complexes, adsorbed to it. The red-ox moieties are attached to many different sites in the porous activated carbon. As a result, the CV curves demonstrating the capacitance of the electrodes vs. potential are expected to be "spread out". Hence, the CV curves that we measure (some of which are presented herein) can be considered as typical responses of composite electrodes containing adsorbed red-ox species on activated carbons. Using organic electrolyte solutions, we could extend the electrochemical window of these electrodes between 1 – (-2.5) V vs. Pt (limited by the solvents reactions, which onset is marked by the rising edges of the CV curves). In this window the Ferroin adsorbed to the carbon matrices can undergo several redox reactions. This is clearly reflected by the reversible peaks of the composite electrodes, which appear at potentials matching the potentials of the unbound redox species. Beside these peaks no other features are seen in the CV curves , what means that there are no side reactions. A very good specific capacitance of 315 F/g was obtained for a weight-balanced two-electrode cell, as seen in Fig. 5b. It should be mentioned that, while usually good rate capability is observed with thin electrodes, and therefor the more important parameter is related to capacity per area. The lateral specific capacity of these electrodes in the experiments described herein was usually close to 3 F/cm^2 .Taking into account a volumetric density of 5.2 cm^3 per gram, the volumetric specific capacity of these electrodes is around 60.5 F per cm^3, what can be certainly considered as a high value for capacitive electrodes. These cells were cycled galvanostatically at constant current densities. The maximum specific capacitance was obtained at currents around 100 mA/g. Doubling the current density led to a reduction in capacity of 20%. At high current densities, around 1 A/g these cells still deliver about 90-95 F/g (Fig. 5d). A typical cycling performance for these systems is presented in Fig. 5c. An impressive retention of 77% of the initial (first cycles) capacity was observed after 9000 cycles.

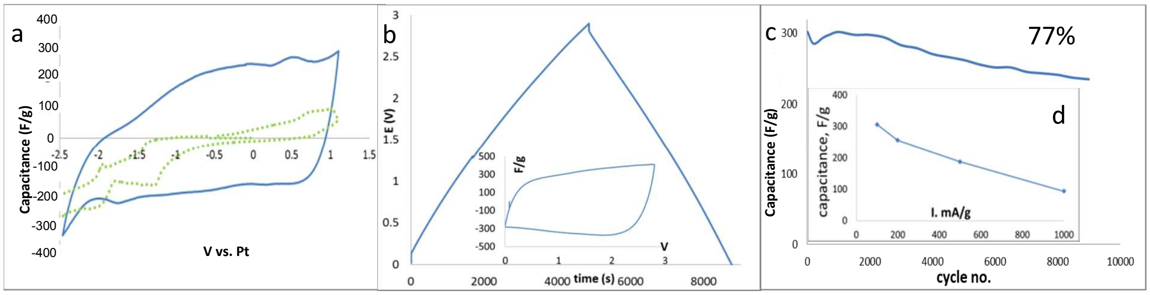

Fig. 5. (a). Typical CV response of three- electrode cells comprising composite Ferroin-chloride/ACF electrodes in 1.4M $TEABF_4$/AN, Pt wire as a quasi-reference electrode. Typical CV curves of a composite electrode (blue line) and unbound Ferroin chloride in the same system on glassy carbon electrodes (dashed green line) are presented. Scan rate=1 mV/s. (b). Galvanostatic charge discharge at constant current of 100 mA/g of weight-balanced two-electrode coin-cell comprising composited ACF/Ferroin electrode as working electrode. (c). Typical results of prolonged galvanostatic cycling of the same systems as in 5b, with a current density= 100 mA/g of electrode's mass. (d). The rate capability response of these two-electrode cells.

Conclusion

We have developed composite electrodes for pseudo super capacitors based on several MOCs with aromatic ligands used as redox active moieties adsorbed to the porous surface of activated carbon fibres (from a commercial source). Composite electrodes were prepared by adsorption of the redox species from both solution and gas phase. It was demonstrated that in the systems selected (carbon, redox moieties, electrolyte solutions) the electrodes are very stable and the redox moieties do not desorb to the solution. It was possible to follow the adsorption processes and their kinetics using uv-vis spectroscopy for the solutions from which the active moieties were adsorbed into the carbonaceous matrices. It was demonstrated that the larger the ligand, containing more aromatic rings, the faster and stronger is the irreversible adsorption process to the activated carbon electrodes. The amount of the MOC loading should be optimized since too high a specific loading may have an adverse effect on the capacity. Some MOCs can be utilized as redox additives for both anodic and cathodic pseudo capacitive reactions. We examined composite electrodes comprising Ferrocene adsorbed to ACF which provided 145 F/g, a gain of 181 % compared to the ACF pure EDL electrodes. More than 10,000 cycles were demonstrated. We also examined composite electrodes comprising Ferroin adsorbed to ACF in non-aqueous acetonitrile based solutions operating within an electrochemical window of 2.7 V , showing specific capacity of > 300 F/g and capacity retention close to 80% over more than 9000 cycles. These electrodes also exhibited very good rate capability. We believe that the approach presented here can lead to the fabrication of new generations of super capacitors that possess much higher energy density than conventional systems, yet demonstrate high rate capability and impressive stability.

Acknowledgments

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