



Charge inversion and colloidal stability of carbon black in battery electrolyte solutions



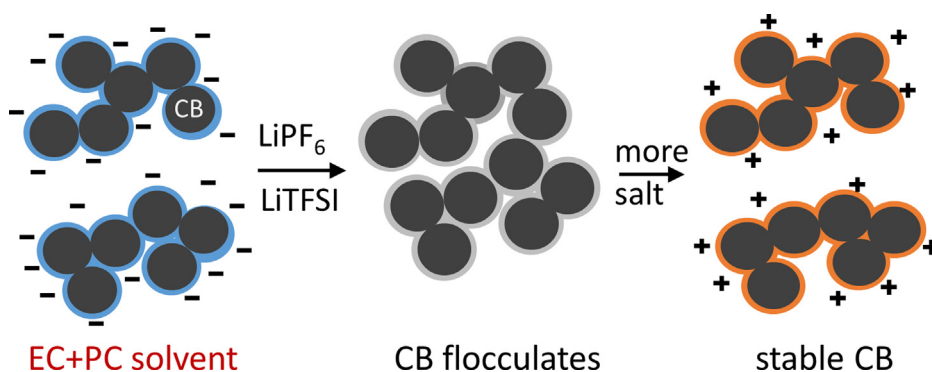
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HIGHLIGHTS

- Specific adsorption of cations on carbon black in carbonate solvent.
- Charge inversion at 2 mM for Li^+ , 20 mM for Na^+ .
- First flocculation regime at 0.1–0.5 mM.
- Re-entrant colloidal stability for Li^+ around 10 mM.
- All systems flocculated at high salt concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

We studied the influence of salt on a commercially available carbon black (Ketjenblack 600, KB) in carbonate solvents commonly applied in rechargeable batteries. Adopting the typically used salts: lithium hexa-fluorophosphate (LiPF_6), lithium bis(trifluoromethane sulfonyl) imide (LiTFSI), as well as sodium hexafluorophosphate (NaPF_6) dissolved in mixtures of ethylene carbonate and propylene carbonate, we investigated both the zeta potential and the flocculation kinetics of the KB particles as a function of salt concentration between 0.01 mM and 1.0 M. Clear evidence was found for the preferential adsorption of cations. In the absence of salt, KB was found to carry a negative surface charge, but this gets neutralized by Li^+ at very low concentrations (~ 1 mM), and by Na^+ at intermediate concentrations (~ 30 mM). In the case of lithium ions, the increased adsorption at higher concentration led to a recovery of the colloidal stability around 3–30 mM, depending on the anion. At high concentrations exceeding 30–100 mM, all salts cause flocculation of the KB particles, due to a reduction of the electric double layer thickness. Since the charge neutralization of the KB by Na^+ takes place in the same concentration regime, no re-entrant stability is found for Na^+ . These findings could have implications in formulation protocols for semi-solid flow batteries, or other systems where an intermediate stable regime could assist mixing and/or structure formation at small length scales.

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1. Introduction

The development of sustainable energy storage systems has become an urgent issue due to the limited amount of fossil

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fuels/natural gas and their huge rate of consumption. Rechargeable lithium ion batteries are one of the most developed in the past few decades and commonly applied in portable electronics, electric vehicles, aerospace devices, etc. [1]. Flow batteries offer more flexibility than solid form batteries, but the energy density of flow batteries is relatively low [2]. A new type, the so-called semi-solid flow battery (SSFB), was invented by MIT and has both the advantage of flow battery's flexibility and the high energy density found in solid batteries [3]. SSFBs differ from other batteries in that their electrodes are dispersions or suspensions, often composed of conductive nanoparticles (CNPs, often carbon black) and electrochemically active particles (EAPs, normally metal oxides which accommodate or release lithium ions during charge and discharge) in electrolyte solutions. Electrons reacting at the redox active particles are conducted by the CNPs to and from current collectors connected to an external circuit.

Since the emergence of SSFBs in 2011, optimization of their composition (EAPs, CNPs, solvent, salt) has been explored [4,5] by measuring the rheological, electrochemical and conductive properties of the fluid electrode in order to understand and improve battery performance. Here colloidal interactions play a crucial role, via their determining influence on both the structure and the dynamics of the fluid. The CNPs, in spite of being present at much lower volume fractions than the EAPs, often dominate both the conductive and rheological behavior of the entire fluid via the formation of a flocculated network. Besides that, the colloidal interactions between active and conductive particles can influence the battery performance [6,7]. However, the situation at present is that only little is known (and much is left to optimize) about the structure and strength of the (EAP surrounded) CNP network, an important reason being that the colloidal interactions between the CNPs are yet to be fully understood.

Both the specific solvent and the used salts (the electrolyte solutions) in SSFBs are the reason for this lack of knowledge. Similar to classical lithium batteries, the electrolytes in SSFBs are typically solutions of Li or Na salts dissolved in carbonate solvents. For example, Li(Na)PF₆, Li(Na)TFSI, Li(Na)BF₄, Li(Na)ClO₄ are used as salts, while ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) are used as solvents. Various combinations of these salts and solvents result in different electrochemical properties [8–10].

In more common solvents such as water, ethanol, hydrocarbons, etc., the behavior of Carbon Black has been better studied. Since van der Waals attractions between CBs are ubiquitous, surface oxidation followed by surface modification generally has to be applied in order to disperse carbon black [11–13]. In aqueous systems, the surface charge likely originates from carboxylate groups, while the extent of screening can be controlled via the salt concentrations. In non-polar solvents there is little screening of the electrostatic interactions, while the surface potential can vary per system (the origin is not always clear). In the battery community, the mixture of EC and PC is recognized as one of the best performing solvents [8,14]. Both EC and PC cannot be ranked amongst conventional solvents, since they are aprotic while having a high dielectric constant. The latter allows dissociation of certain salts up to high concentrations (as needed for achieving high conductivity). In turn, the dissociated ions can change both the surface potential and the electric double layer thickness. This could mean that the electrostatic interactions bear similarity to those in aqueous systems. However, even in that case there might be practical differences in the behavior at low salt concentrations, because the sensitivity of carbonate solvents to impurities is quite high.

A particular process that could modify the electrostatic particle interactions, is specific ion adsorption. Depending on the signs of the native surface charge and the adsorbing ion, even reversal of the surface charge is possible. This phenomenon has been studied

for a variety of colloids [15–20], including many oxides in aqueous environments [15–17]. Sign reversal of the zeta potential induced by alkali metal cations such as Li⁺ and Na⁺ has been found in a few cases (e.g. [21]), while for protons it is a well-known phenomenon, also in non-aqueous solvents [15].

In this paper we focus on the principal aspects of the colloidal stability of Carbon Black suspensions in electrolyte solutions containing the same ingredients as in a typical SSFB. We chose three electrolyte solutions, namely LiTFSI, LiPF₆ and NaPF₆ dissolved in a 1:1 binary mixture of EC and PC. Measurements of the zeta potential as a function of salt concentration are combined with determinations of the time-dependent average hydrodynamic (aggregate) diameter with Dynamic Light Scattering (DLS). By starting the DLS experiments with the suspensions in a non-flocculated state, we measure the flocculation rate, and calculate the stability ratio. Combining the observations from the two types of experiments allows us to draw conclusions about the ion adsorption and stabilization mechanism.

2. Theory

In this section we summarize the approach and key equations as used to measure the stability ratio of the KB particles, as a function of salt concentration. The initial stage of the flocculation of particles with uniform size and shape can be described via the second-order reaction:

$$\frac{dN}{dt} = -kN^2 \quad (1)$$

where N is the concentration of the non-flocculated particles and k is the flocculation rate constant. Early stages of the flocculation process can be analyzed by measuring the average hydrodynamic radius (R_h) with DLS as a function of time [22]. The linear dependence of R_h on time in this regime allows to determine dR_h/dt , which is proportional to the flocculation rate. The average hydrodynamic radius is calculated using the Stokes–Einstein equation:

$$D = \frac{k_B T}{6\pi\eta R_h} \quad (2)$$

where D is the measured diffusion coefficient, η the viscosity of the medium and k_B the Boltzmann constant and T the absolute temperature. Unlike many aqueous salt solutions, the viscosity of solutions in carbonate solvent depends significantly on the salt concentration: it nearly triples when the concentration of LiTFSI [23], LiPF₆ [24] and NaPF₆ [25] reaches 1 M (see also Appendix 1). This is of importance when calculating R_h , but also for the proper normalization of the flocculation rate: in more viscous media, the diffusion-limited flocculation of particles takes longer. This aspect, expressed by the factor $K_{Smol} = 8k_B T / 3\eta$ in the Smoluchowski equation is taken into account by multiplying η_r and dR_h/dt , where ($\eta_r = \eta_{sa}/\eta_{so}$ with η_{sa} the viscosity of the salt solution and η_{so} likewise for the solvent). The stability ratio [26,27] is then defined as:

$$W = \frac{[d(R_h \times \eta_r)/dt]_{\max}}{d(R_h \times \eta_r)/dt} \quad (3)$$

This quantity equals 1 (regardless of the viscosity) in all cases of unhindered flocculation. Repulsive interactions give rise to an energy barrier, which slows down the flocculation and hence increases W . In the limit where the particles do not flocculate at all, W approaches infinity.

We remark that the use of dR_h/dt to calculate the stability ratio relies on the assumption that R_h increases linearly with time, which can only be expected in the early stages of the flocculation [28]. This implies that the analysis should be performed well within the so-

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