

Short communication

Relationships between processing, morphology and discharge capacity of the composite electrode

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Abstract

The cycled capacity of $\text{Li}_{1.1}\text{V}_3\text{O}_8$ based positive electrodes varies between 100 and 250 mAh g^{-1} ($C/5$ rate, 3.3–2 V) depending on the processing parameters. The initial volatile solvent concentration has a strong impact on the distribution of the electrode constituents. For a concentration below the optimal one, the mechanical energy available for mixing is insufficient to overcome viscosity forces and to reach a good dispersion of the constituents in the bulk of the electrode. Above the optimal concentration, settling of the $\text{Li}_{1.1}\text{V}_3\text{O}_8$ and carbon black particles in the low viscosity suspensions creates a concentration gradient. In these two cases the electrochemical performance are degraded. The viscosity of the electrode slurry must be systematically adjusted since the grain size and density depend on the active material.

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1. Introduction

The battery active electrode materials are routinely evaluated via the electrochemical performance of their composite electrodes that are prepared with standard formulations and routine processing conditions. The relationship between electrochemical responses and these experimental variables are not commonly explored. Only a few studies deal with the effect of the processing conditions on the composite electrode morphology and electrochemical performance [1–7]. Here, we study lithium trivanadate ($\text{Li}_{1.1}\text{V}_3\text{O}_8$) based positive electrodes and we use a pre-plasticized poly(methyl methacrylate) (PMMA) with the ethylene carbonate–propylene carbonate electrolyte solvent (EC–PC) [8–9]. Different composite electrodes were realised by the solvent casting technique. The solvent concentration was varied. Rheology measurements are used to understand the mixing step of the electrode elaboration. Weight loss measurements and settling rate measurements are used to follow the drying step.

2. Experimental

A home-synthesized $\text{Li}_{1.1}\text{V}_3\text{O}_8$ (at 580 °C [10]) was used as the active material, and carbon black (Super-P, noted CB,

ERACHEM), as a conductive agent. The binder was plasticized PMMA ($M_w = 996,000 \text{ g mol}^{-1}$, Aldrich). A mixture of ethylene carbonate (EC)/propylene carbonate (PC) (1:1, w/w) was used as the plasticizer. Battery-grade chemicals such as EC (Aldrich), PC (Aldrich), THF (purity >99.9%, SDS), and lithium bistrifluorosulfonimide (LiTFSI, 3 M) were all used as received.

The composite positive electrodes were prepared by following a classical solvent route where THF was used as the dispersing medium. The $\text{Li}_{1.1}\text{V}_3\text{O}_8$ and carbon black powders were dispersed in the binder solution to form a suspension using a magnetic stirrer for 12 h. The suspension was then spread on aluminium disks (1 cm^2) for electrochemical measurements or on adapted supports. These composite films were dried at room temperature for 2 h to evaporate the solvent, dried further under vacuum at 50 °C for 1 h. The dry composite electrode was constituted of 73% (w/w) of $\text{Li}_{1.1}\text{V}_3\text{O}_8$, 8% (w/w) of carbon black and 19% (w/w) of PMMA. When the binder was plasticized, the liquid additive represents 20% (w/w) of the dry matter. For electrochemical measurements they were then transferred under dry argon atmosphere in a glove box ($\text{H}_2\text{O} < 1 \text{ ppm}$) for battery assembly.

Two-electrode SwagelokTM test cells, using the composite positive electrodes, a porous paper soaked with the electrolyte as the separator and metallic lithium as the negative electrode were assembled in the glove box. A mixture of EC/PC (1/1, w/w) containing 1 M LiTFSI was used as liquid electrolyte. All

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voltages given in the text are reported versus Li^+/Li . Cell cycling was performed at 25°C , monitored by a VMPTM system in galvanostatic mode. The voltage range used was 3.3–2 V. We used a standard galvanostatic procedure corresponding to the insertion of one lithium ion in 2.5 h during the discharge and one lithium during 5 h during the charge.

Scanning electron microscopy (SEM) imaging of composite electrodes was performed on gold-palladium sputtered samples using a JEOL JSM 6400F apparatus. Cryogenic fracture was used to image the section of the samples.

Rheological properties were measured at 25°C under steady shear between 1000 and 1 s^{-1} . We used a controlled rate viscosimeter (VT550 HAAKE) equipped with a standard Couette cell that contains the sample in a 0.9 mm concentric cylindrical gap between a cup, 12.45 mm diameter, and a bob, 10.65 mm diameter and 31.95 mm length. Temperature was controlled by a circulating water bath, typically to within $25 \pm 0.2^\circ\text{C}$.

Sedimentation rates were determined for electrode slurries poured into closed tubes. The fall of the interfacial plane between the electrode slurry and the clear supernatant was monitored as a function of time at a temperature of 25°C . The drying kinetics of the electrode suspension was followed with gravimetric analysis, through monitoring weight percentage loss as a function of time at a temperature of 25°C .

3. Results

3.1. Electrochemical performance and morphology of the dried electrode

Table 1 gives the composition of the electrode slurries. Note that the composition of the electrode suspension includes the volatile solvent. Then, the volume ratio of the active material, carbon black, binder and plasticizer vary because the solvent concentration varies. However, after evaporation of the volatile solvent, the electrode composition is the same, whatever the initial volatile solvent concentration, i.e. 58.4% (w/w) of $\text{Li}_{1.1}\text{V}_3\text{O}_8$, 6.4% (w/w) of carbon black and 15.2% (w/w) of PMMA and 20% (w/w) of EC–PC. Moreover, please note that the quantity of EC–PC added to plasticize PMMA is negligible compared to the total quantity that is added with the liquid electrolyte at the battery assembly. As a matter of fact, we estimate that it is lower than 0.1% (w/w). Then, the dried matter composition of the composite electrode in the battery, during electrochemical evaluation, is in fact 73% (w/w) of $\text{Li}_{1.1}\text{V}_3\text{O}_8$, 8% (w/w) of carbon black and 19% (w/w) of PMMA. Electrochemical performance of composite electrodes prepared with

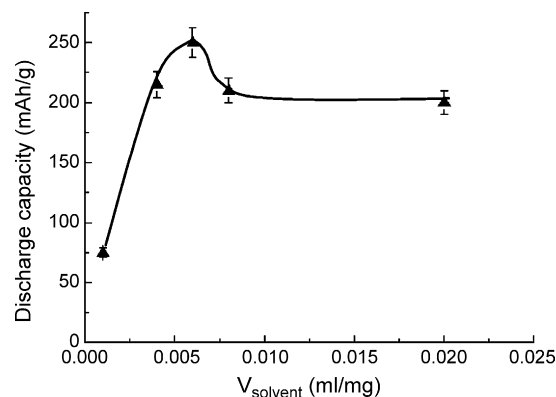


Fig. 1. Evolution of the discharge capacity with the solvent concentration expressed in ml mg^{-1} of dried material.

varying amounts of solvent is shown in Fig. 1. The solvent concentration is expressed in ml mg^{-1} of dried matter. There exists an optimal concentration for which the discharge capacity of the electrode is the largest. SEM observations of the composite electrodes were done below the optimal solvent concentration, at the optimum and above the optimum. Below the optimum, the composite electrode microstructure is not homogeneous. Some pure PMMA zones and some aggregates of $\text{Li}_{1.1}\text{V}_3\text{O}_8$ grains can be detected (see Fig. 2a). Such microstructure can explain the poor performance of this composite electrode. The $\text{Li}_{1.1}\text{V}_3\text{O}_8$ grains within the aggregates are not in direct contact with the carbon black network and cannot be reached by electrons. Part of the active material does not participate, therefore, to the electrochemical reaction. Above the optimal solvent concentration, the composite electrode microstructure is not homogeneous either. A $25\ \mu\text{m}$ thick polymer “skin” at the surface of the electrode could be observed (see Fig. 2c). This morphology could result from a sedimentation phenomenon in the low viscosity slurry. In the case of the optimal solvent concentration, the morphology is homogeneous and all the constituents appear uniformly distributed (Fig. 2b).

3.2. Study of the mixing step

The rheological behaviour of the electrode slurry was studied for different solvent concentrations (Fig. 3). The less concentrated slurry ($0.008\ \text{ml mg}^{-1}$) exhibits a Newtonian behaviour while the more concentrated one ($0.002\ \text{ml mg}^{-1}$) exhibits a high yield stress τ_0 . The electrode slurry with the optimal solvent concentration exhibits an intermediate behaviour with a low but measurable yield stress τ_0 . Table 1 gives the τ_0 values.

Table 1
Composition and characteristics of the electrode suspensions

Solvent concentrations (ml mg^{-1})	Suspension composition and characteristics (% , v/v)					τ_0 (mPa)	U_s ($\mu\text{m min}^{-1}$)
	$\text{Li}_{1.1}\text{V}_3\text{O}_8$	CB	PMMA	EC–PC	THF		
0.002	8.2	1.6	6.1	7.6	76.5	29,550	0
0.006	3.2	0.6	2.4	3.0	90.7	3,000	60
0.008	2.8	0.5	1.9	2.3	92.9	0	140

The solvent concentration is expressed in ml mg^{-1} of dried matter (DM).

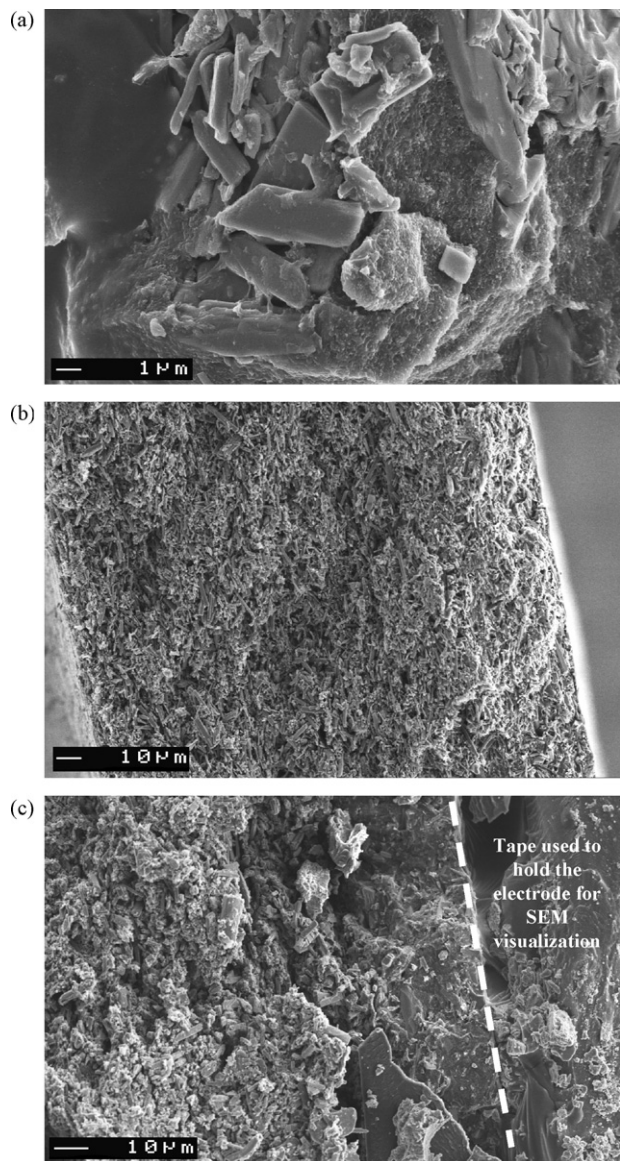


Fig. 2. SEM observations of composite electrodes elaborated with various THF concentrations: (a) 0.002 ml mg⁻¹, (b) 0.006 ml mg⁻¹, and (c) 0.008 ml mg⁻¹.

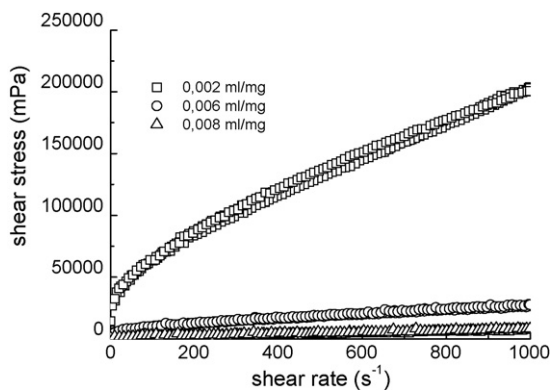


Fig. 3. Evolution of the shear stress with the shear rate of the electrode slurries for different solvent concentrations (0.002, 0.006, and 0.008 ml mg⁻¹).

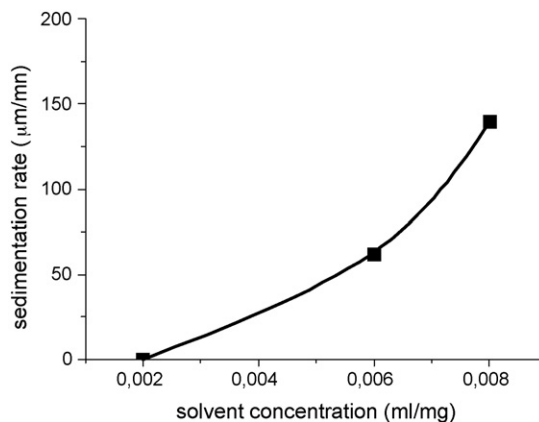


Fig. 4. Experimental sedimentation rate as a function of the solvent concentration.

These rheological properties are typical of weakly flocculated systems [11]. The presence of attractive forces between the particles leads to a connectivity throughout the system, giving rise to a weak network. The yield stress is a manifestation of the network structure and means that a minimum stress is required to induce sample flow. With decreasing the solvent concentration, i.e. increasing the particles volume fraction, the connectivity throughout the system grows and the yield stress increases. In the dilute slurry only isolated clusters exist and $\tau_0 = 0$. Below the optimal solvent quantity, the low discharge capacity and poor homogeneity of the composite electrode correlates with a high yield stress, related to connectivity throughout the slurry which opposes to the flow and mixing of the constituents.

3.3. Study of the drying step

The settling of electrode slurries poured into closed tubes was visualized and monitored with a video camera. Settling rates, U_s , were determined by measuring the distance Y between the surface of the settling slurry and the clear supernatant as a function of the time t . The U_s values calculated from the initial slopes of the $Y(t)$ curves are reported as a function of the solvent concentration in Fig. 4. U_s increases when the solvent concentration increases. Theoretically, sedimentation can be evaluated thanks to the relation established by Stokes [12]. For spherical grains, the sedimentation rate, U_s , is given by

$$U_s = \frac{g}{18\eta_a}(\rho_g - \rho_A)d^2 \quad (1)$$

where d is the diameter of the grains, ρ_g the grain density, ρ_A and η_a the suspending medium density and viscosity, respectively, and g is the gravitational acceleration. Note that the PMMA/THF polymer solution constitutes the suspending medium. In agreement with experiments, Eq. (1) predicts that U_s increases when the solvent concentration increases because the polymer volume fraction ϕ_{PMMA} decreases. As a matter of fact, polymer solution viscosity increases when the polymer volume fraction increases. Similar equations can be derived for the more complicated shapes of grain like the $\text{Li}_{1.1}\text{V}_3\text{O}_8$ sticks or the carbon black fractal aggregates [13]. They predict for the sedimenta-

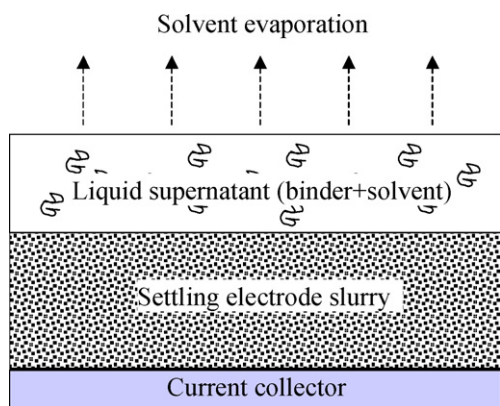


Fig. 5. Schematic description of the drying step.

tion rate the same type of dependence with respect to the grains diameter and density, and to the suspending medium viscosity and density.

The electrode slurry prepared with 0.008 ml mg^{-1} exhibits a very high settling rate. When the electrode is solvent casted, a liquid supernatant must form in which the polymer will concentrate upon solvent evaporation to form a polymer “skin” at the top of the dried electrode, as observed by SEM (Fig. 2c). This rich polymer layer implies moreover depletion of this constituent in the bulk, which could explain the decrease of the electrochemical performance. Poor electronic wiring of the active material grains embedded in the rich polymer-layer should result from thick PMMA layers in between the particles [6]. Depletion of the polymer at the bottom of the composite electrode could result in low adhesion to the current collector or limited liquid electrolyte uptake in this region [13]. The electrode slurry prepared with 0.006 ml mg^{-1} exhibits a moderate but significant settling rate. However, no polymer “skin” could be detected. The following argument could explain this apparent contradiction. During drying, both the particles settling and the solvent evaporation occur simultaneously, as schematically described in Fig. 5. The two effects could counterbalance to prevent formation of a liquid supernatant.

4. Conclusion

As a summary, the initial volatile solvent concentration has a strong impact on the distribution of the electrode constituents

within the dried composite material and on the electrochemical performance. The best discharge capacity is obtained for a critical solvent concentration, which is rationalized in terms of rheological behaviours. For a concentration below the optimal one, the mechanical energy available for mixing could be insufficient to overcome viscosity forces and to reach a good dispersion of the constituents in the bulk of the electrode. Above the optimal concentration, settling of the active material and carbon black particles in the low viscosity suspensions can create a concentration gradient. In these two cases the electrochemical performance is degraded. The solvent concentration or solid loading must be systematically adjusted to optimize the electrode performance whenever one wants to evaluate a new active material or electrode formulation. The density and the diameter of the active material and carbon black particles are important parameters. When their density and their size increase, the sedimentation rate increases.

The solvent nature and especially its evaporation behaviour is another important parameter, which we study in another paper [13]. It appears the crucial point is the competition between particles settling and solvent evaporation to prevent the formation of a liquid supernatant appears.

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