OPTIMIZE LITHIUM-ION BASED BATTERY SLURRIES STABILITY USING THE HANSEN APPROACH

APPLICATION TO REFORMULATION USING EFFICIENT GREEN SOLVENTS

Context

Formulating stable particle suspensions is of great interest for academic and industrials as it allows to enhance the properties and the lifetime of their products. Among industrial fields which are interested in suspension stability, Energy is one of the most currently attractive especially with battery slurries. Overall, the choice of the stabilization medium is the key factor to avoid particle agglomeration during slurries storage which can lead to injectability problems during battery coating steps. In addition of the stability efficiency, there are a constant need of greener solvent exhibiting lower toxicity and higher biodegradability to satisfy product regulatory requirements evolution. A such search can be carried out using predictive methods as Hansen Parameters (HP). The aim of this note is to demonstrate that effective reformulation of a Lithium-ion ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) based battery slurry with greener solvents can be proceed by coupling HP and TURBISCAN technology.

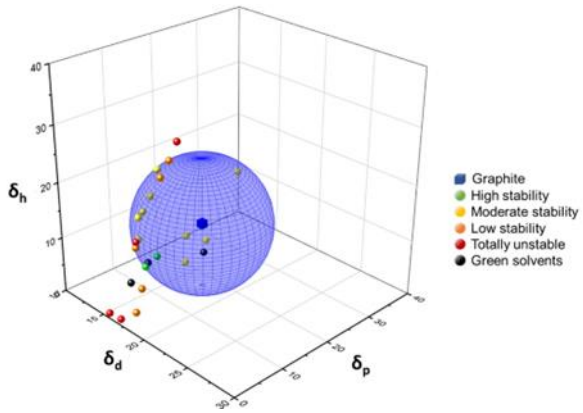


***Figure 1** : Hansen sphere obtained for $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ particles (FIT=1, no solvent wrong in, no solvent wrong out)*

Definiton

The semi-empirical Hansen's approach, which has been historically developed to predict the solubili ty of molecules, can be adapted to describe the particles stability in various solvents. This approach is based on the decomposition of the Hildebrand parameter δ, linked to the binding energy between two particles, into three different parameters δ_d, δ_p and δ_h describing respectively non-polar, polar and hydrogen interactions between the particle surface and the dispersion media as follow:

$$\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2}$$

Considering these non-polar, polar and hydrogen components, each particle or solvent can be represented by a point in a 3D-space with these components as coordinate values named HP coordinates. The stability of the particle under study is evaluated considering a range of solvents with known HPs exhibiting large variation in these 3D-space and followed by a ranking of the tested solvents as good or poor stabilization media. The border between good and poor solvents allows to build a sphere with a center corresponding to the HP coordinates of the particle as well as a radius R0. If a solvent is situated inside the sphere of the particle, it can be considered as a good stabilization media.

Inversely, a solvent situated outside the sphere should poorly stabilize the suspension. Considering the distance Ra between the determined HP coordinates of the particle ($\delta_{D,p}$; $\delta_{P,p}$; $\delta_{H,p}$) with the one of another solvent ($\delta_{D,s}$; $\delta_{P,s}$; $\delta_{H,s}$), it is quite easy to estimate the Relative Energy Difference, named RED, which indicates if the chosen solvent should give a stable (RED < 1) or an unstable suspension (RED ≥ 1) as follow:

$$RED = \frac{R_a}{R_0} \quad with$$

$$R_a = \sqrt{4.(\delta_{D,p} - \delta_{D,s})^2 + (\delta_{P,p} - \delta_{P,s})^2 + (\delta_{H,p} - \delta_{H,s})^2}$$

TURBISCAN: How it works

TURBISCAN technology is based on Static Multiple Light Scattering and consists of sending a light source on a sample to acquire a backscattered and transmitted signal all over the height of a sample in its native state. By repeating this measurement over time at adapted frequency, the instrument enables to monitor physical stability of a sample without dilution.

To compare the stability of different suspensions in a quantitative way, the TURBISCAN Stability Index (TSI) can be used. The TSI is a number calculated at time t by summing up all temporal and spatial variations in a considered zone:

$$TSI(t) = \frac{1}{N_h} \sum_{t_i=1}^{t_{max}} \sum_{z_i=z_{min}}^{z_{max}} |BST(t_i, z_i) - BST(t_{i-1}, z_i)|$$

However, as the solvents can exhibit quite different values of densities and viscosities, a direct comparison of the macroscopic stability appears not so relevant due to the strength of the gravitational stability which can be higher for low viscosity solvents and lower for high viscosity ones. To obtained reliable comparison results, the contribution of the gravitational stability should be withdrawn by normalization according to the values of density and viscosity of each solvent. In that view, the Relative TURBISCAN Stability Index (RTSI) should be used to remove the contribution given by the solvent viscosity and density in the macroscopic stability. Accordingly, as the RTSI do not consider the gravitational stability, it becomes a descriptor of the suspension colloidal stability:

$$RTSI(t) = TSI(t).\left(\frac{\eta}{\rho_p - \rho_s}\right)$$

With η the dynamic viscosity of the solvent (mPa.s), ρ_p the particle density (taken as 2.16 g.cm-3 for $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ [1]) and ρs the solvent density ($g.cm^{-3}$)

The real advantage to use the TURBISCAN technology in the Hansen approach is to discriminate in an accurate way the tiny stability variation of solvents tested as good dispersion media, which is quite difficult by conventional observation. Such measurements allow generating a Hansen sphere which is more precise and restrictive than the ones obtained through visual characterization of samples as it is classically realized.

Methods for evaluating suspension stability by HDP approach

Macroscopically stable Graphene dispersed in 1mL of Lithium-ion ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) based battery slurry at 42wt% in NMP (Nanomyte BE-45 NCA Slurry from NEI Corp.) has been diluted in 19mL of miscible solvent and dispersed according to a mechanical stirrer at 1000rpm during 15 minutes. The following table 1 indicates the Hansen parameters of each mixture of solvents calculated by averaging the Hansen parameters of the individual solvents by volume.

***Table 1**: List of the 21 solvents tested to build the Hansen Sphere of the Lithium-ion based battery slurry under study*

Solvents	δ_d	δ_p	δ_h
NMP	18.00	12.30	7.20
5%v NMP/95%v Acetone	15.63	10.50	7.01
5%v NMP/95%v THF	16.86	6.03	7.96
5%v NMP/95%v DMF	17.43	13.63	11.10
5%v NMP/95%v H2O	15.63	15.82	40.55
5%v NMP/95%v MeOH	14.87	12.30	21.55
5%v NMP/95%v EtOH	15.91	8.98	18.79
5%v NMP/95%v DMSO	18.38	16.20	10.05
5%v NMP/95%v Isopropanol	15.91	6.41	15.94
5%v NMP/95%v 1-Propanol	16.10	7.08	16.89
5%v NMP/95%v Formamide	17.24	25.51	18.41
5%v NMP/95%v 1-Hexanol	16.01	6.13	12.24
5%v NMP/95%v 1-Octanol	16.10	5.37	11.00
5%v NMP/95%v Chloroform	17.81	3.56	5.78
5%v NMP/95%v Ethylene glycol	17.05	11.07	25.06
5%v NMP/95%v Toluene	18.00	1.95	2.26
5%v NMP/95%v Propylene glycol	16.86	9.55	22.50
5%v NMP/95%v 2-Butoxyethanol	16.10	5.46	12.05
5%v NMP/95%v Glycerol	17.43	12.11	28.20
5%v NMP/95%v Cyclohexane	16.86	0.62	0.55
5%v NMP/95%v Heptane	15.44	0.62	0.36

Following the dispersion step, the sample was immediately closed, and its stability was measured during 2 hours at 25 °C in a TURBISCAN Tower. To score the different solvents, a dedicated RTSI scale is used as it described in a quantitative way the colloidal stability comparison of the different suspensions tested. Obtained results are presented in figure 2. The solvent was scored from 4 when a totally unstable suspension is obtained (RTSI>10), to 1 for the obtainment of a suspension with a high colloidal stability (RTSI<0.1).

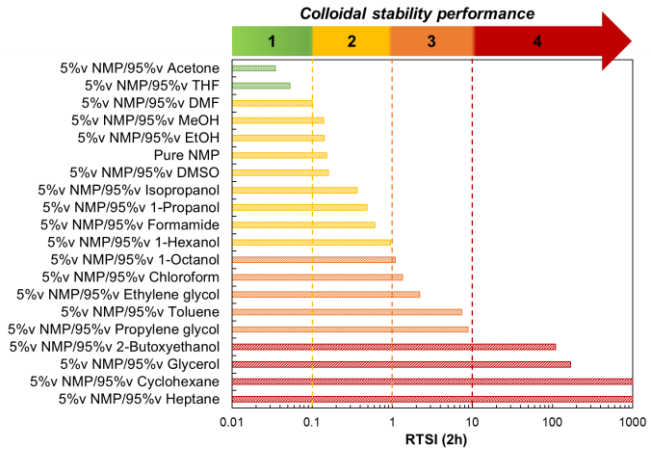


***Figure 2** : RTSI obtained after 2 hours for the 21 solvents tested to stabilize $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ particles*

Calculation of HP stability sphere

Having the RTSI values allows scoring each solvent toward its ability to stabilize $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ particles and so building the corresponding Hansen sphere by repeated calculation and iteration using an adapted software like HSPiP as highlighted by figure 3.

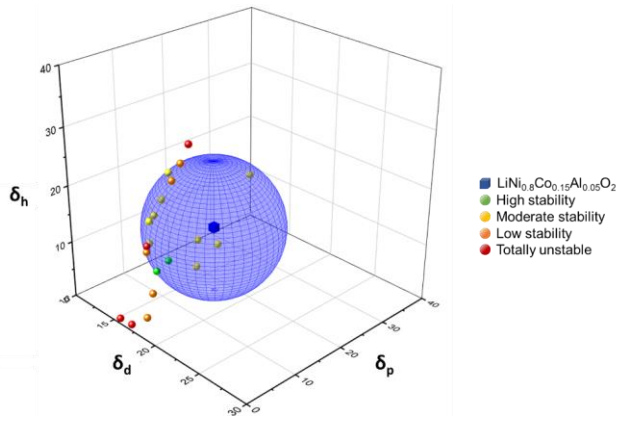


***Figure 3**: Hansen stability sphere obtained for $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ particles (FIT=1, no solvent wrong in, no solvent wrong out)*

From the localization of the sphere center by the software, the Hansen parameters of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ particles are easily obtained as well as the stability sphere radius.

The values obtained are the following ones:

$$\delta_D = 17.7\ MPa^{1/2} \quad \delta_P = 16.8\ MPa^{1/2}$$
$$\delta_H = 12.3\ MPa^{1/2} \quad R_0 = 11.7\ MPa^{1/2}$$

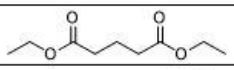
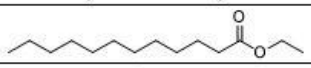
From these values obtained, it is quite easy to calculate the RED and predict if another green solvent will be a good or a poor stabilization media (*i.e.* inside or outside the stability sphere) according to its own Hansen parameters. A classification of potential green solvents regarding stabilization properties can be also predicted considering that the lower is the RED value, the more stabilized suspension should be obtained.

Using this methodology, three different green solvents has been chosen according to their position in the Hansen 3D space from the $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ stability sphere:

- Diethyl glutarate (δ_d=16.3, δ_p=7.0, δ_h=7.8)
- Ethyl laurate (δ_d=16.2, δ_p=3.4, δ_h=5.3)
- δ-Butyrolactone (δ_d=18.0, δ_p=16.6, δ_h=7.4)

The structure of these solvent as well as the RED of their corresponding mixtures with the Lithium-ion based battery slurry are displayed in the following table 2. In the same way, the position of these corresponding mixtures compared to the corresponding stability sphere in the Hansen 3D space are highlighted in figure 1 (black dots).

***Table 2** : Common names, chemical structures and RED values of the three green solvents targeted through the Hansen approach*

Green solvents	Chemical structure	RED
Diethyl glutarate		0.93
Ethyl laurate		1.28
δ-Butyrolactone		0.43

According to their RED values, two solvents (Diethyl glutarate and δ-Butyrolactone) are expected to be interesting stabilizing media for $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ particles and one (Ethyl laurate) which should have bad stabilizing properties. Figure 4 gathers colloidal stability results through RTSI as well as RED values of these three green solvents with $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ particles.

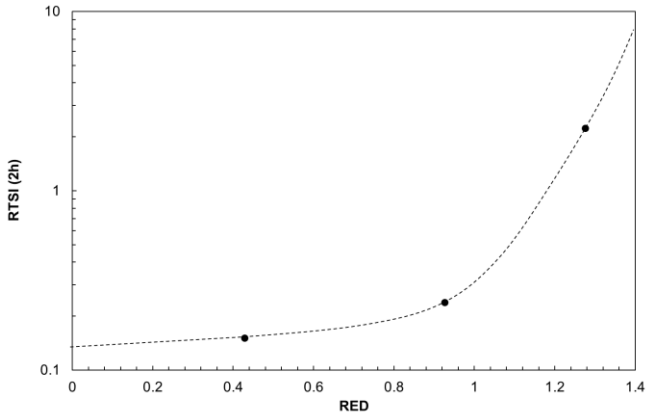


***Figure 4** : Colloidal stabilities (RTSI) in function of RED values of the three formulated green solvent Lithium-ion slurries.*

According to this figure, the more reduced is the RED value, the better will be the colloidal stability. In that way, Diethyl glutarate and δ-Butyrolactone appear to have quite good colloidal stabilizing properties with RTSI values of 0.24 and 0.15 respectively. For Ethyl laurate, as it is situated outside the Hansen stability sphere due to a RED value higher than 1, the resulting colloidal stability is even worse with a RTSI value of 2.24 which situated this green solvent into the class of low stability solvents. This result validates clearly the prediction through the Hansen model, and indicates also that this empirical approach is well adapted for the green solvent reformulation of real Lithium-ion based battery slurries. Another interest is also the choice of green solvents exhibiting non negligeable values of viscosities which can highly reinforce the suspension macroscopic stability compared to the colloidal ones, as well as solvents exhibiting quite low fusion temperature allowing a good curing during the battery manufacturing process.

Conclusion

TURBISCAN technology experiments have been performed to quantify and compare the effect of the stabilization media on the stability of a Lithium-ion based battery slurry. The TURBISCAN technology, through the measurement of the colloidal stability, allows classifying the different solvents tested and is well adapted to the Hansen approach for predicting better and greener stabilization media. In that way, this approach finds a direct application in predicting greener solvents to optimize battery slurries regarding the product regulatory requirements evolution. As the TURBISCAN technology can either discriminate the stability and the dispersibility of particles, the Hansen approach could be also employed to characterize the dispersibility properties of solvents with application not only dedicated to battery slurries but also for other formulation fields such as paints & inks, foods and beverages or pharmaceutical and nutraceutical formulations.