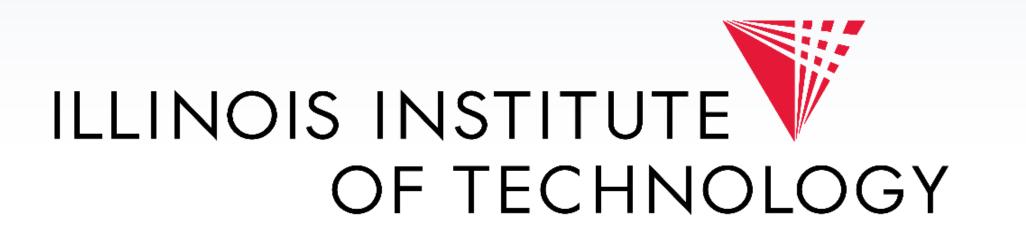


Engineering Nanofluid Electrodes: Thermophysical & Electrochemical Properties of Ni(OH)₂ Nanoparticles



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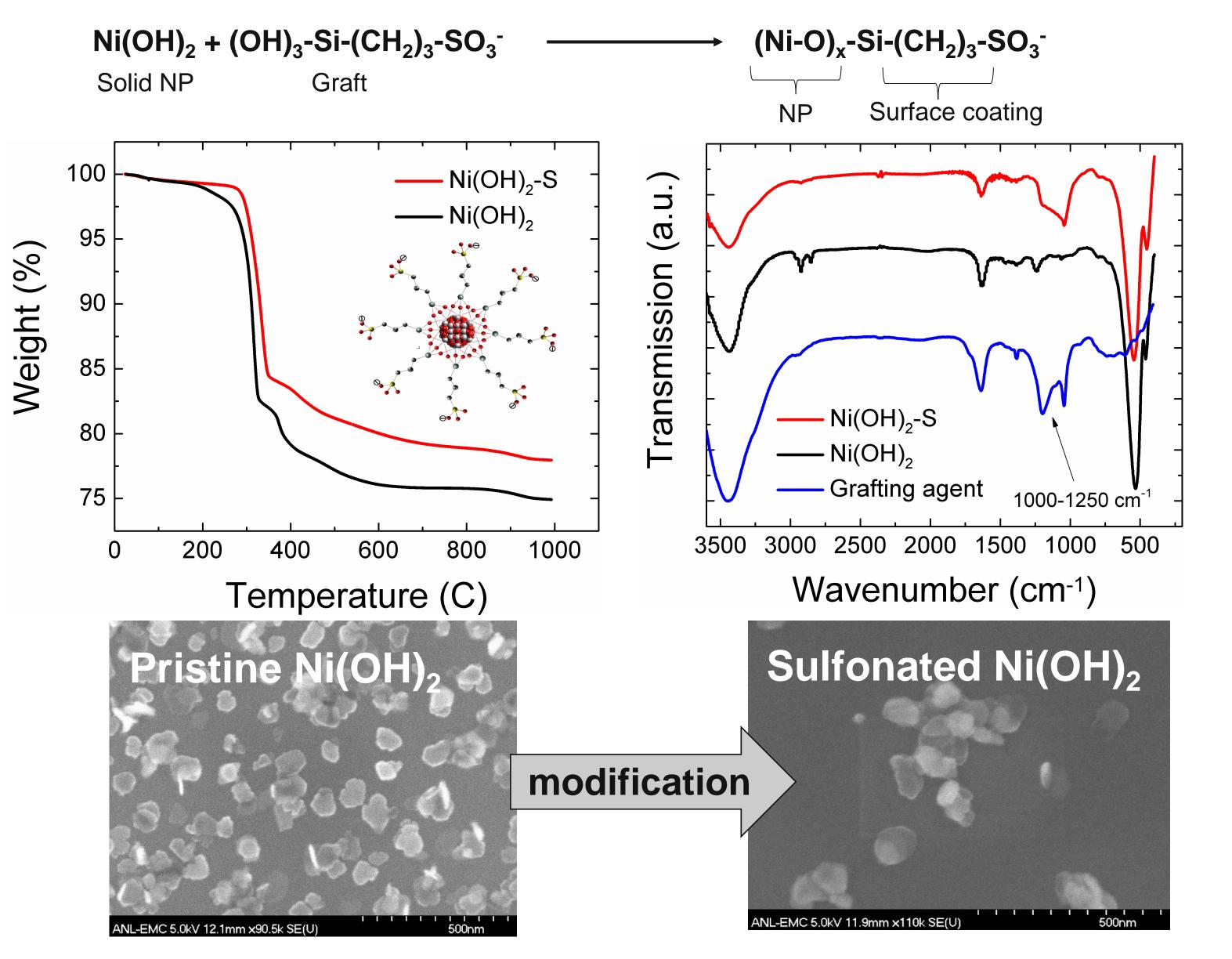
Introduction

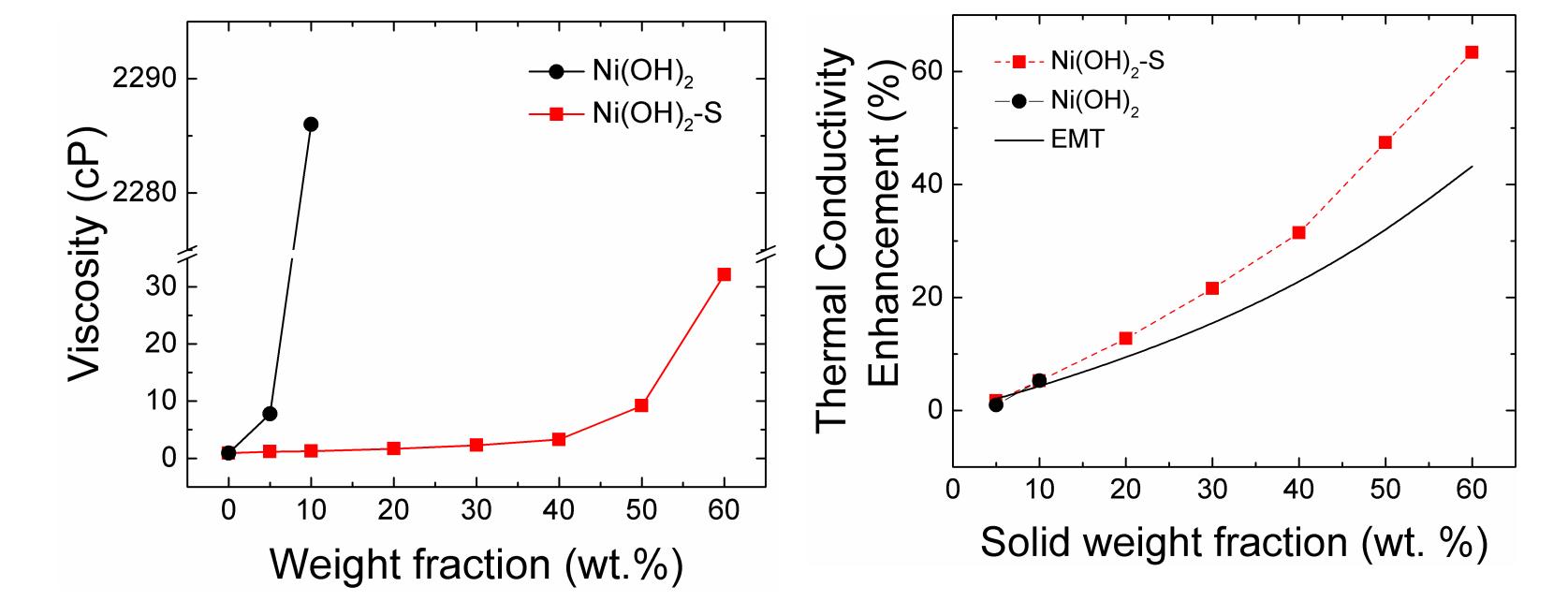
Nanofluid electrodes or nanoelectrofuels have significant potential in the field of flow batteries, as at high loadings of solid battery active nanoparticles, their energy density can be orders of magnitude higher than in traditional redox flow battery electrolytes. Nanofluid electrodes must have a manageable viscosity at high particle concentrations (i.e. easily pumpable) and must exhibit good electrochemical activity towards charge and discharge reactions. Engineering of such nanofluid electrodes involves development of new and unique approaches to stabilization of nanoparticle suspensions. In this work, we demonstrate a surface modification approach for nickel hydroxide nanoparticles (Ni(OH)₂) that allows control of viscosity of nanofluids at high solid loading, while simultaneously retaining electrochemical activity. (Ni(OH)₂) has known use as a cathode material in aqueous batteries.

Viscosities of the pristine $(Ni(OH)_2)$ and modified $(Ni(OH)_2-S)$ nanofluids are presented relative to the base fluid as a function of nanoparticle loading. Maximum concentration of 60 wt.% was achievable for the Ni(OH)_2-S nanofluids with a viscosity of 32 cP. While suspensions with 10 wt.% of the Ni(OH)_2 nanofluid had viscosity exceeding 2200 cP under the same conditions.

Surface modification

For surface modification, pristine Ni(OH)₂ nanoparticles were treated with a silane based grafting moiety in aqueous media to obtain sulfonated Ni(OH)₂. Thermogravimetric (TGA) analysis revealed < 3 wt.% loading of the grafting moiety, which corresponds to a near monolayer coverage. SEM imaging of the particles before and after surface modification do not show considerable changes indicating a relatively thin surface coating. Distinct peaks in the 1000-1250 cm⁻¹ range of the FTIR spectra correspond to the Si-O and Si-Metal stretches indicating the presence of the grafting moiety in the modified sample but not in the pristine material.





Experimental thermal conductivity of $Ni(OH)_2$ -S nanofluids show linear increases with particle loading with values similar to those predicted by effective medium theory (EMT). Enhancements as large as 60% were observed over the base fluid thermal conductivity. The deviations observed at larger concentrations are likely due to the increasing degree of nanoparticle agglomeration. Agglomeration provides extended paths for heat conduction within solid particle ensembles, which are more efficient than solid/liquid/solid paths.

Electrochemical Testing

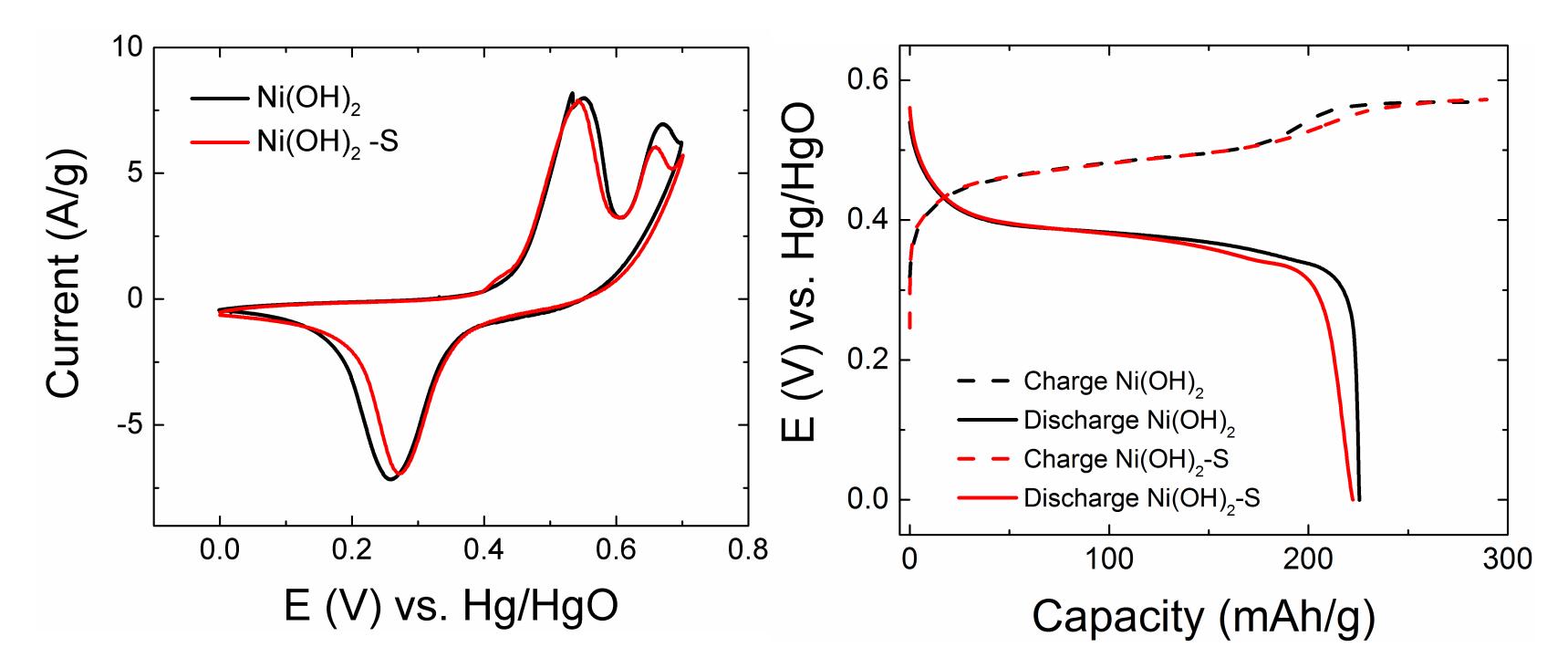
Cyclic voltammograms of solid casted electrodes from both $Ni(OH)_2$ and $Ni(OH)_2$ -S

Nanofluid Properties

Nanofluids were prepared using pristine and modified nanoparticles in aqueous solutions containing 30 mM KOH/10 mM LiOH. Dynamic Light Scattering (DLS) technique was used to study the agglomeration state of nanoparticles within the nanofluids. Number distribution spectra shows peaks at 1366 nm for Ni(OH)₂-S particles and 117nm for Ni(OH)₂. This indicates that in case of pristine nanoparticles, large agglomerates are present in the suspension, while individual particle exist in the Ni(OH)₂-S nanofluid.

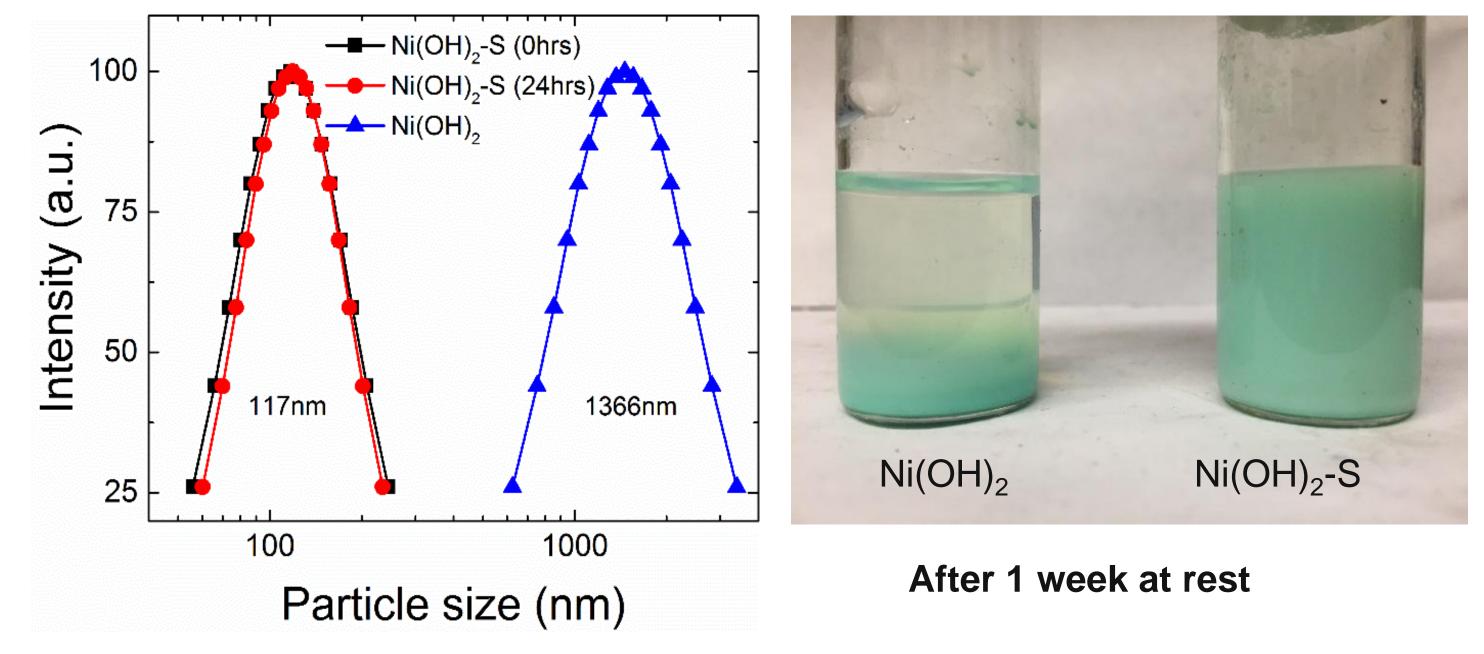
reveal reversible redox chemistry centered at 0.4V vs. Hg/HgO in aqueous 5.5 M LiOH. Galvanostatic testing of the electrodes (C/3 charge; C/3 discharge) revealed a comparable maximum discharge capacity of 225 mAh/g for both samples, indicating minimal effects of the surface coating on electrochemical performance.

 $Ni(OH)_2 + OH^2 \longrightarrow Ni(OOH) + H_2O + e^2$ Theoretical Capacity : 289 mAh/g



Summary

A scalable single step procedure for the surface grafting of small organic molecules onto



Zeta potential measurements demonstrated values of -30 ± 3 mV for pristine Ni(OH)₂ and -48 ± 2 mV for sulfonated Ni(OH)₂-S particles at pH 10. The higher surface charge on Ni(OH)₂-S nanoparticles prevents particle agglomeration resulting in good particle dispersion and superior colloidal stability.

nickel hydroxide nanoparticles is demonstrated. Stable dispersions with up to 60 wt. % of solid loading in alkali aqueous electrolytes are prepared with a maximum viscosity of 32 cP at room temperature. Suspensions of surface modified Ni(OH)₂ particles also show up to 60% enhancements in thermal conductivity, as compared to base electrolytes. Electrochemical testing of the pristine and modified nanomaterials in solid casted form showed comparable electrochemical activity with a discharge capacity of 225 mAh/g. Future testing will involve electrochemical testing of nanofluids.

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