Effect of ‘water-in-salt’ electrolytes in the electrochemical hydrogen evolution reaction of carbon nanotubes

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Abstract

Super-concentrated electrolytes based electrochemistry is an emerging trend in electrochemical processes (Borodin et al 2020 Joule 4 69–100), where unprecedented properties were reported recently. Such an ‘electrolyte engineered approach’ can find applicabilities in modern batteries and catalysis. Here we report the use of such high concentration lithium ions (Li$^+$) containing electrolytes for enhancing the electrocatalytic hydrogen evolution (HER) performance of carbon nanotubes (CNTs), contrary to that observed with platinum. Different types of CNTs, namely metallic multi-wall (MWCNTs) and semiconducting single wall (SWCNTs), are tested towards the Li$^+$ effect in the HER performance and similar trends are obtained. Further, different lithium salts having counter ions such as TFSI$^-$, OTf$^-$, ClO$_4^-$, Cl$^-$, and OH$^-$ are also tested to verify the mechanism, and the role of Li$^+$ in the HER augmentation of CNTs is established. The studies are conducted in different electrolytes having a range of pH values too (0–13), and the cation induced CNT’s HER enhancement is generalized. This study shows that even the sluggish HER kinetics of CNTs in alkaline medium can be augmented by such an electrolyte engineering approach where catalyst’s surface do not undergo any permanent modification. Further, such electrodes are found to be highly stable towards the long term HER performance.

Carbon nanotubes (CNTs, both multi-wall (MWCNTs) and single wall (SWCNTs)) were sought after for several applications due to their unique properties such as high surface area, quasi-one dimensional structure, micro-structure dependent electronic properties, and mesoporosity [1, 2]. The investigation of the previous two-decades also examined their potential in catalysis—both as ‘true catalysts’ and catalytic supports [3]. But, due to the presence of unavoidable metallic impurities residing in CNTs—where those were used as catalysts for the growth, the inherent catalytic activities of CNTs were highly questioned in the literature [4, 5]. But, the everlasting demand for the replacement of precious metals from the existing energy systems, CNTs and their hybrids were highly explored for different heterogeneous catalytic applications [3, 6, 7]. Further, recent study shows that the residual impurities become important in deciding the catalytic properties only in CNTs having two or three walls [4]. It is also observed that SWNCTs can have enhanced catalytic activities compared to MWCNTs as a result of the presence of nanographitic edges [8, 9]. MWCNTs are in general inactive towards heterogeneous catalytic reactions, and engineering them via different means, including covalent coupling, has shown to bring activity to them [3, 10]. In this scenario, here we suggest the possibilities of their intrinsic catalytic activity be tuned via ions in the supporting electrolytes, such as lithium ions (Li$^+$).

Hydrogen evolution reaction (HER) via water splitting is considered as the greener route towards the production of techno-economically viable high energy density fuel, H$_2$(g), and different catalysts were explored in the past as alternates to the benchmarked platinum (Pt) [11]. The ideal metal-hydrogen binding energy (thermoneutral, $\Delta G_{\text{H}} \approx 0$ eV) with large number of adsorption sites is assumed as the best descriptor for predicting the HER activity of a material, and Pt along with other Pt group metals lie on the
apex of the volcano plot, making them as ideal for HER process [12]. Recently we have shown that engineering the number of active sites per area by forming dendritic structures can be used to enhance the HER activity of MoS₂ atomic layers, thereby climbing their position in HER volcano plot [13]. Similarly, atomic doping is proven to enhance the catalytic activity of many nanoscale structures, including CNTs and graphene, and such modifications can be considered as permanent electrode/catalyst modification [14, 15].

On a different attempt, we have also pursued the modification of the HER activities of metals via supporting ions, such as Li⁺ [16–18]. In those studies, it is shown that high concentration electrolytes based catalysis can affect the inherent electrode catalytic activity of the metal quite drastically, while such modifications do not make any permanent alteration to the surface. i.e. the electrode (working electrode used for the catalysis) does not undergo any permanent modification via doping or intercalation after the high concentration salts (sometimes called ‘water-in-salt’ type electrolytes) based electrolysis, and its inherent activity will be retained while doing the same electrode in further normal electrolytes based catalysis. It is shown by our recent study that metals like gold (Au), iron (Fe), and nickel (Ni) can augment their HER electrocatalytic activity with the increase in Li⁺ ions (systematically increase with concentration), while Li⁺ ions suppress the HER activity of iridium (Ir) and Pt [18]. Such a tunability in the HER activities of metals are proven to be due to the metal hydrogen binding energy variations due to the presence of Li⁺, which further affects their positions in the HER volcano plot. The ability of Li⁺ to tune the hydrogen evolution reactivity of Pt by modifying metal-hydrogen bond energy is further supported by another recent study by Weber et al [19]. According to their findings, the hydrogen evolution reactivity of Pt (both polycrystalline Pt and high surface area carbon supported Pt nanoparticles) is the highest in 0.1 M LiOH among same concentration of LiOH, NaOH, and KOH due to non covalent interaction between Li⁺ and Pt, where it changes arrangement of water molecules and hence the energetics of adsorbed hydrogen on Pt surface. Effect of supporting cations at low concentrations in tuning the HER kinetics of metals has been widely studied in the recent past, and a detailed discussion on the same can be seen in our previous work [18]. Some of the recent seminal works include the one by Bandarenka et al, where they measured the influence of alkali metal cations in the electrical double layer capacitance of Pt (111) and Au (111) electrodes [20]. They found that in the presence of electrolytes of 0.05 M AMClO₄ (where the AM can be Li⁺/Na⁺/ K⁺/ Rb⁺/ Cs⁺ at pH 6), the local effective concentrations of the cations at the electrode surface can be ~ 80 times higher than their bulk concentrations [20]. Further, in another work, they reported the differences in the HER behaviors of different metals in presence of these alkali metal ions [21]. Hence, these works show that spectator species such as Li⁺ ions can have an important role in controlling the kinetics of heterogenous reactions such as HER. Further, in the limit of ‘water-in-salt’ like electrolytes, the water hydration sphere near the electrode changes drastically from that of the low salt conditions [19], and hence unprecedented properties can be expected in these limiting concentrations.

Here we report such an effect of Li⁺ on a non-metallic system, namely CNTs, and generalized the effect of Li⁺ in CNT’s HER properties. This phenomenon has been tested in different types of CNTs having different electronic properties [metallic (MWCNTs) as well as semiconducting (SWCNTs) of chirality (7,6) and (6,5) having diameter of 0.7–1.1 nm] and dimensions or aspect ratio [MWCNTs of two different vendors are tested, those from CheapTube.com have 10–30 µm length and 20–30 nm diameter and those obtained from Sigma-Aldrich.in have 5–7 µm length and 110–170 nm diameter].

Lithium salts having different counter ions such as TFSI⁻ (bis(trifluoromethanesulfonyl)imide), OTF⁻ (trifluoromethanesulfonate), ClO₄⁻ (perchlorate), Cl⁻ (chloride), and OH⁻ (hydroxide) are used for the present investigation. The HER activity variation with varying salt concentration is tested in electrolytes having different pH values too. Different electrochemical techniques such as linear sweep voltammetry (LSVs) and electrochemical impedance spectroscopy (EIS) are used to establish the HER activity variations of CNTs in these different salts containing electrolytes.

Details of the sample preparation and electrochemical studies are given in the supporting information. In a nut shell, a three-electrode set up is used for the electrochemical HER studies where the working electrode is modified with CNTs containing inks (the ink preparation is also explained in the supporting information). This investigation used two types of MWCNTs (from CheapTube denoted by MWCNT 1 and from Sigma-Aldrich indicated by MWCNT 2) and two types of SWCNTs (both from Sigma Aldrich)—denoted by their chirality. The scanning electron microscope (SEM) images of all the CNTs and the Pt electrode (3 mm diameter) are shown in the supporting information, figures S1(A)–(E) (available online at stacks.iop.org/ JPhysEnergy/2/034001/mmedia). The tubular structure of the CNTs is evident from the images. The energy dispersive x-ray spectra (EDX) and EDX mapping of the pristine CNTs are shown in figures S2 and S3, indicating that the metal impurities in all the CNTs are less than 0.1 atomic %. In figure S4, micro-Raman spectra of all the CNTs are shown and the major vibration modes are identified, which is in tune with the reported ones [3]. The purified CNT ink is drop casted on a 3 mm glassy carbon (GC) working electrode, where the CNT ink has been prepared by the following method: 4 mg of CNTs are dissolved in a mixture of
water, Naftion, and ethanol (750 µl H₂O + 250 µl ethanol + 50 µl 5 wt% Naftion (binder)) and sonicated for 30 min to form a complete dispersion. 2 µl (kept constant for all the experiments) of this ink is drop-casted on the 3 mm GC electrode. The loading of the sample on the GC electrode is found to be ~ 0.108 mg cm⁻².

The HER LSV polarization curves for Pt and MWCNT 1 are shown in figures 1(A) and (B), respectively. It is clear from these figures that the HER activity of Pt decreases with increasing LiTFSI concentration from 1 M to 20 M, which is in tune with our previous findings [16,18]. But with increasing LiTFSI concentration from 1 M to 20 M, the HER activity of MWCNT 1 is found to be increased, as shown in figure 1(B), and the systematic variations in the HER activities of these two electrodes with different LiTFSI concentrations are shown in figure S5. A similar variation observed in the HER activity of MWCNT 2 is discussed later.

To establish these HER changes further, EIS studies are conducted and the corresponding Nyquist plots are shown in figures 1(C) and (D). The best fitted Randles circuit for the obtained plots is shown in the insight of figure 1(C). Two different types of ions namely H⁺ (inner Helmholtz plane) and Li⁺ (outer Helmholtz plane) are present in the electrical double layer region and the circuit represents all the steps in the HER process [22]. The EIS circuit elements consist solution resistance (Rₛ), the double layer capacitance (Q), adsorption resistance (R), capacitance due to the specific ions (H⁺/OH⁻) C_DL and charge transfer resistance (R_CT). The variations in the Rs, C_DL, and R_CT of different electrodes and electrolytes are summarized in the table S1 of the supporting information.

Suo et al were initially reported that LiTFSI based ‘water-in-salt’ type electrolytes can be used to construct aqueous electrolyte based batteries with enhanced water stability window of ~ 3 V [23]. The LiF layer formed on the anode prior to the HER due to the electrochemical cycling will block the electron transfer to H⁺, and hence enhance the water stability via this kinetic barrier. Hence LiF layer formation will happen in cases where LiTFSI is used in high concentration for electrolysis. The LiF formation during the electrolysis with LiTFSI salt containing electrolytes was observed in our recent study too, where we used gold (Au, polycrystalline) as a working electrode [16]. The formation of LiF on Au surface was established using x-ray photoelectron Spectroscopy based analyses, supporting information figure S9 of the reference 16 and Infrared spectroscopy, supporting information figure S8 of the reference 18. Here, the EIS studies on both the
electrodes, Pt and MWCNT 1, indicate the enhanced Rs, suggesting the formation of passive LiF layer. But the high frequency charge transfer resistances of Pt and MWCNT 1 with high and low concentration LiTFSI showed a stark contrast in the trend. With increasing LiTFSI concentration, initially the Rs decreases due to increasing number of ion carriers but at higher concentrations, Rs increases as the number of ion pairs increases [24, 25], which can be observed in figures 1(C) and (D), and table S1.

The Rs values for Pt and MWCNT 1, when using both 1 M and 20 M LiTFSI, increase from 106 Ω to 369 Ω and 99 Ω to 210 Ω, respectively. The HER charge transfer resistance (R_{CT}) for Pt increases from 14 Ω (1 M LiTFSI) to 450 Ω (20 M LiTFSI) whereas the double-layer capacitance (C_{DL}) due to inner Helmholtz plane decreases from 216 μF (1 M LiTFSI) to 50 μF (20 M LiTFSI), which suggests that with increasing LiTFSI concentration the HER activity of Pt becomes unfavorable. The normalized (with respect to geometric surface area of Pt electrode, 0.07 cm²) C_{DL} of Pt is found to be 3.1 mFcm⁻² in 1 M LiTFSI and 0.7 mFcm⁻² in 20 M LiTFSI, where the previous report on the C_{adsorbed} value on Pt (111) surface was 0.5 mFcm⁻² in the under potential deposition (UPD) voltage region, irrespective of the pH of the electrolyte [26]. The larger capacitance values in the present study can be due to accumulation of Li⁺ ions in the double layer region, as suggested by Bandarenka et al [20, 21]. But in the case of MWCNT 1, the R_{CT} decreases from 9185 Ω (1 M LiTFSI) to 5133 Ω (20 M LiTFSI) whereas the C_{DL} increases from 28 μF (1 M LiTFSI) to 64 μF (20 M LiTFSI), which suggests that with increasing LiTFSI concentration the HER activity of MWCNT 1 becomes favorable and the inner Helmholtz plane increases, as it is observed for Au, Fe, and Ni [18]. A deeper understanding on the double layer formation with high salt concentration can obtain only with in situ studies such as infrared spectroscopy, and such studies are in progress [27].

In order to verify the effect of Li⁺ on the HER of CNTs in other pH values, the aqueous electrolyte is replaced with 0.05 M H₂SO₄ (pH = 0) and 0.1 M NaOH (pH = 13). Though 20 M LiTFSI solubility could be achieved in 0.1 M NaOH, only 2.5 M solution of LiTFSI was achieved in 0.05 M H₂SO₄. The HER activity of MWCNT 1 is found to be augmented (in terms of both onset potential lowering and current density enhancement) with increasing LiTFSI concentration from 0 to 2.5 M LiTFSI for 0.05 M H₂SO₄ and 1 to 20 M LiTFSI for 0.1 M NaOH, as shown in figures S6(A) and (B). Further the enhanced HER activity of MWCNT 1 in 0.1 M NaOH is confirmed by replacing LiTFSI with LiOTf—another high solubility Li salt, as shown in figure S7. It is evident from the EIS measurements (figures S6(C) and (D), and table S1) that the HER R_{CT} values of MWCNT 1 decrease in both the pH conditions with increase in LiTFSI concentrations. However C_{DL} values for MWCNT 1 increase from 6 μF to 23 μF and 228 μF to 421 μF when LiTFSI concentration increases from 0 M to 2.5 M in 0.05 M H₂SO₄ and 1 M to 20 M LiTFSI in 0.1 M NaOH, respectively. These observations suggest that with increase in LiTFSI concentration in both acidic and alkaline pH, the HER
activities of MWCNT 1 become favorable and the inner Helmholtz layer increases, as it is observed previously in neutral pH. But on comparing the HER performance in presence of Li$^+$ in acidic, neutral, and alkaline conditions, one can see that the effect is highest in alkaline conditions, as shown in figures 2 and S8. Ram Subbaraman et al. had studied the enhanced hydrogen evolution activity of Li$^+$-Ni(OH)$_2$-Pt interfaces and have found that Li$^+$ can induce the destabilization of HO-H bond [28]. In alkaline conditions, Li$^+$ is known to interact with H$_2$O more strongly and hence Li$^+$ modifies the inner Helmholtz plane in alkaline conditions. This modification in the double layer is reflected in the differences in the double layer capacitance in alkaline (228 $\mu$F to 421 $\mu$F) and acidic (6 $\mu$F to 23 $\mu$F) conditions. Hence as Ram et al. Reported [28], the presence of Li$^+$-OH-H complexes in the compact portion of the double layer in alkaline conditions can be the reason for such drastic changes in the double layer capacitance and hence for the observation of highest Li$^+$ ion effect in alkaline conditions. But it has to be noted that the alkaline HER process is more complex than that in acidic conditions due to water as the adsorbate instead of protons [29, 30], and further, the nature of hydration sphere of Li$^+$ changes at high salt concentrations. Hence more insight is needed to be acquired to understand the observed changes in the alkaline HER kinetics of CNTs with Li$^+$ concentrations.

To further confirm the observed effect, other types of CNTs namely MWCNT 2 and SWCNTs of two different chirality (7,6) and (6,5) are also studied in similar manner. The HER activities of all the CNTs (MWCNT 2, SWCNT (7,6), and SWCNT (6,5)) are found to be increased with LiTFSI concentrations in a similar fashion as that observed in MWCNT 1, as shown in the figures S9 and S10 (EIS of SWCNT (7,6) in alkaline conditions).

To further establish the role of Li$^+$ ions in the observed phenomenon, other lithium salts such as LiClO$_4$, LiCl, and LiOH are also used as supporting electrolytes in the HER electrolysis. When LiClO$_4$ concentration is varied from 1 M to 5 M in 0.1 M NaOH, the HER activity of both the MWCNT 1 and SWCNT (7,6) are found to be enhanced enormously, as it is shown in figure 3. Similar enhancements in the HER activities of both MWCNT 1 and SWCNT (7,6) are observed with increasing LiCl too, while increasing its concentration from 1 M to 5 M in initial alkaline pH condition, as shown in figure S11. To further ensure the effect of Li$^+$, the HER activity is tested with LiOH electrolytes with varying concentration from 0.1 M to 2 M in water changing the pH from 13 to 14, and the data is shown in figure S12. It is evident that though the pH of the
solution was enhanced, the HER activity is found to be augmented. The results shown in figures 3 and S12, and that summarized in table S1 indicate that irrespective of the counter ions present, the HER activity of both the types of the tubes - metallic MWCNT 1 and SWCNT(7,6), become favorable with Li\(^{+}\) concentrations.

Further confirmation of Li\(^{+}\) ion effect in the HER is obtained from the LSV measurements of SWCNT (7,6) in NaClO\(_4\) and NaCl in 0.1 M NaOH with varying the concentration from 1 M to 5 M (figure S13). It is clear from the HER LSV polarization curves that the HER activity of the SWCNT (7,6) is not altered (similarly other tubes too) with the NaClO\(_4\) or NaCl concentrations.

Among the MWCNT 1 and SWCNT (7,6), SWCNT (7,6) shows better HER activity as it is shown in figures 4 and S14, and it can be due to the presence of graphitic edges in SWCNTs, as it is explained in the introduction. Further, both the CNTs show similar HER activity in similar amount of different lithium salts (5 M LiClO\(_4\) and LiCl) containing 0.1 M NaOH.
The HER activity of SWCNT (7,6) is found to be ‘poor’ in 0.1 M NaOH with high onset potential (440 mV vs. RHE) and over potential (740 mV) for 10 mAc\textsuperscript{-2} current density, figures 4(A) and (B). But with increasing LiClO\textsubscript{4} concentration to 5 M in 0.1 M NaOH, the onset potential decreases to 240 mV vs. RHE whereas the over potential to achieve 10 mAc\textsuperscript{-2} current density decreases to 460 mV. The EIS measurements show a decrease in the R\textsubscript{CT} value for SWCNT (7,6) from 2561 \Omega (in 0.1 M NaOH) to 245 \Omega (in 5 M LiClO\textsubscript{4} plus 0.1 M NaOH), cf Figure 4(C) and table S1.

Tafel slope analysis is a powerful technique in determining the reaction mechanism of hydrogen evolution reaction [31, 32]. The HER tafel slope of Pt in 0.1 M NaOH is found to be 56 mVdec\textsuperscript{-1} (figure 4(D)), which is similar to its reported values [33]. The tafel slope of SWCNT (7,6) decreases from 363 mVdec\textsuperscript{-1} in 0.1 M NaOH to 122 mVdec\textsuperscript{-1} in 5 M LiClO\textsubscript{4} in 0.1 M NaOH. The exchange current density of SWCNT (7,6) in 0.1 M NaOH is calculated as 1.33 \times 10\textsuperscript{-4} Acm\textsuperscript{-2} where it increases to 4.3 \times 10\textsuperscript{-4} Acm\textsuperscript{-2} in 5 M LiClO\textsubscript{4} in 0.1 M NaOH. These observations suggest that the HER activities of CNTs, both MWCNTs and SWCNTs, can be augmented with supporting ions such as Li\textsuperscript{+}, while such effect is not observed with Na\textsuperscript{+} ions. Further, the same electrode of (MWCNT1 and SWCNT(7,6)) used for high concentration electrolyte based electrolysis is studied in 0.1 M NaOH and the data is shown figure S15. It is clear from the LSV curves that complete reversal of the HER activity is observed in both the cases indicating that the Li\textsuperscript{+} do not make any permanent alteration to the catalyst’s surface and which is supported by miro-Raman spectra of SWCNT (7,6) before and after cycling in 5 M LiClO\textsubscript{4} in 0.1 M NaOH, shown in figure S16.

Stability in the HER performance is an important parameter to evaluate the performance of a catalyst. Chrono-potentiometry experiment is performed for 20 h at 10 mAc\textsuperscript{-2} current density. Figure 4(E) shows that the over potential to achieve 10 mAc\textsuperscript{-2} current density increases negligibly from 460 mV to 500 mV for SWCNT (7,6) after 20 h whereas that for Pt increases from 160 mV to 440 mV, indicating the better stable HER performance of the Li\textsuperscript{+} ions modified SWCNT (7,6) electrode. Further, table S2 shows the comparison of the HER performance of different important graphitic carbon systems so far reported. Most of the reports on the HER performance of CNTs and graphene are in acidic medium, while those in alkaline medium show high over potential, indicating the sluggish HER kinetics of CNTs in higher pH electrolysis. But the present study shows that the comparable over potentials can be achieved in alkaline medium too with the modification using Li\textsuperscript{+} ions. The modifications in the CNT-proton adsorption energy with Li\textsuperscript{+} may be the possible reason for such a drastic change in the catalytic activities with lithium salt concentration variation, similar to that observed in different metals [18]. But, a multi-scale simulation assisted theoretical understanding of the phenomenon is needed to justify this proposition and such studies are in progress.

In conclusion, the tunability in the electrochemical HER performances of CNTs with Li\textsuperscript{+} ions containing salts is established and the HER performances of CNTs are found to be augmented with the salt concentration, even with the different pH values of the electrolyte. Different types of CNTs are tested towards this phenomenon where both metallic as well as semiconducting nanotubes of different aspect ratio exhibited similar trend in HER with Li\textsuperscript{+} ions. Further, effect of anions in the HER engineering is tested using different types of lithium salts namely—LiTFSI, LiOTf, LiClO\textsubscript{4}, LiCl, and LiOH, and a similar augmentation in the HER properties of CNT is observed. This indicates the minimal role of anions in the observed phenomenon while the LiTFSI and LiOTf based electrolytes have the LiF formation, as observed by Suo et al. Despite the presence of LiF kinetic barrier for proton reduction, the HER performances of CNTs are found to be enhanced with the higher concentration of LiTFSI and LiOTf. Finally, the observed phenomenon is found to be not making any permanent alteration to the catalyst surface, and HER stability of the CNTs in ‘super-concentrated’ electrolytes is found to be very high in comparison to that of Pt. The HER performances of CNTs with ‘water-in-salt’ type electrolytes are found to be enhanced even in alkaline conditions, where otherwise their performance is sluggish in nature. This work opens wide possibilities in engineering the HER performances of graphitic systems, namely graphene, CNTs, and other hybrid structures, via a simple modification of electrode-electrolyte interface, where these graphitic materials are envisaged as stable catalysts for future energy technologies [34–36].

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