Supporting Information

Investigating 2D WS₂ supercapacitor electrode performance by Kelvin Probe

Force Microscopy

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Capacitive vs Intercalation/Deintercalation Charge storage

There may be multiple types of charge storage mechanisms for different electrodes (or sometimes on the same electrode) of a device. Hence it is important to distinguish between the capacitive charges stored and the charges stored by the diffusion-controlled ion insertion (intercalation/de-intercalation mechanism). The two can be distinguished by performing CV at different scan rates (sweep rates) and then using Cottrell's equation which shows the dependence of the current response on the sweep rate and is given by¹

 $i = av^b$...(1)

b value calculations

In the above equation, i is the current response at a specific scan rate v (in V/s) at the given voltage (V) and a and b are adjustable parameters. At a certain voltage (V), i follows a unique characteristic with the different scan rates v, which are very closely related to the mechanism through which charges are being stored. The value of the exponent of v, which is b is the key to determine the mechanism of charge storage i.e., whether it is diffusion-controlled (solid-state ion diffusion) or non-diffusion controlled (capacitive). The value of b is well defined for each of these two conditions but may transition in-between, if both the mechanism exists simultaneously to some extent.

If the charge storage mechanism is diffusion controlled, the current becomes proportional to the square root of the scan rate v and follows the equation^{1, 2}

$$i = nFAC^*D^{1/2}v^{1/2} (\alpha nF/RT)^{1/2}\pi^{1/2}\mathbb{P}(bt) \qquad \dots (2)$$

where *n* is the number of electrons exchanged in the electrode reaction, *F* is the Faraday constant, *A* is the surface area of the electrode, C^* is the surface concentration of the electrode material, *D* is the chemical diffusion coefficient, *v* is the scan rate in V/s, α is the transfer coefficient, R is the molar gas constant, T is the temperature, and the $\mathbb{Z}(bt)$ function shows the normalized current for a completely irreversible system as indicated by the cyclic voltammetry response. Here, in this condition, the current, *i* becomes diffusion-controlled and if we compare equation (2) with (1), we observe that the value of *b* is 0.5. Hence, we can say that as the value of *b* approaches 0.5 in the Cottrell's equation, the charge storage and the current become more and more diffusion controlled. For a completely diffusion-controlled charge storage system, the current *i* will follow the exponential dependency on the scan rate of $av^{0.5}$.

But if the charge storage mechanism is a non-diffusion-controlled, which includes all types of capacitive charge storage (i.e., both EDLC and pseudo-capacitance), then the current i becomes directly proportional to the change in scan rate v and follows the equation given as

$$i = vC_dA \qquad \dots (3)$$

where, C_d is the capacitance. When we compare this equation (3) with the Cottrell's equation (1), we can observe that the value of *b* is equal to 1. Hence, we can say that as the value of *b* approaches to 1, the charge storage mechanism becomes more and more of capacitive type i.e. non-diffusion-controlled and is completely capacitive when the value of *b* is exactly 1.

In order to understand the nature of the charges stored and their proportions in a device, cyclic voltammetry has to be performed at different scan rates. Using the concepts discussed above, and Cottrell's equation (1), how the current changes with different scan rates at a certain voltage V should be monitored. Thus, the value of *b* needs to be determined, which lies between $0.5 \le b \le I$. This provides us whether the current and charges stored are capacitive or by solid state ion diffusion. To determine this value of *b*, if log on both sides in the Cottrell's equation are taken, we get log i = blogv + a. Now, if we plot a curve between log i vs log v, for a given voltage V, a straight line should result and the *b* value for that specific voltage will be given by the slope of that straight line. Once we get the *b* value on a specific voltage V, by doing similar calculations at different voltage values, we can also plot a curve between the b value and the operational voltage range (V) of the device.



Figure S1: Shows the value of b vs V (for pristine WS₂ electrode), where b value ranges from $0.5 \le b \le 1$. The b- value approaches a minimum of 0.6 at around 0.2 V, which signifies that at around 0.2 V, the charge storage mechanism becomes highly diffusioncontrolled. For all other values of V, the charge storage remains shared between diffusioncontrolled and capacitive mechanism.

For our pristine WS₂ electrode, how *b* values are calculated from *log i vs log v* curve is shown in figure S2. For demonstration purpose, these curves have been plotted and compared for two voltage values of 0.2 V and -0.1 V. The slope (*b* value) calculated at 0.6 V comes out to be 0.60 (closer to 0.5) which is indicative of more intercalation/de-intercalation type charge storage, while the slope (*b* value) at -0.1 V is calculated to be 0.77, which is indicative of capacitive charge storage mechanism, with lesser diffusion-controlled contribution. After calculating *b* values at different voltages, a *b* vs V curve has been plotted and shown in figure S1. It shows that the *b* value ranges from $0.5 \le b \le 1$ and it approaches a minimum of 0.6 at around 0.2 V, which signifies that at around 0.2 V, the charge storage mechanism becomes highly diffusion controlled. For all other values of V, the value of *b* lies between 0.5 and 1, which means that at these voltages, the charge storage is a hybrid of diffusion-controlled and capacitive mechanism.



Figure S2:Plot showing how e b value can be determined by plotting the curves between log i and log v, for a pristine WS₂ electrode. This plot is supposed to be a straight line. The slope of this line gives the value of b. For demonstration purpose, these curves are plotted and compared for two voltage values of 0.2 V and -0.1 V. The slope (b value) calculated at - 0.1 V is 0.77 which indicates more capacitive type charge storage, while the slope (b value) at 0.2 V is calculated to be 0.6 which indicates a more diffusion-controlled mechanism.

k value calculations

In a very similar analysis, the current at any given potential (V), is a combination of capacitive charges stored (i.e., non-diffusion-controlled) and the charges stored via the diffusion-controlled process. Thus, the current originating from these two mechanisms can also be divided into two categories: (a) capacitive current and (b) current from solid-state ion diffusion.³ Therefore, mathematically using the Cottrell's equation, the total voltammetry current can be written as

$$i(V) = k_1 v + k_2 v^{1/2} \dots (4)$$

where i(V) is the CV current at any given potential V, k_1v is the contribution of current originating from capacitive type charge storage (both EDLC and pseudocapacitance), and $k_2v^{1/2}$ is the current originating from solid-state ion diffusion. In order to calculate the value of k_1 and k_2 equation (4) can be rearranged in the following way

$$\frac{i(V)}{v^{1/2}} = k_1 v^{1/2} + k_2 \qquad \dots (5)$$

Experimentally, current at different potentials can be collected from CV measurements, for i(V)

varying scan rates v, and then a curve can be plotted between $\overline{v^{1/2}}$ and $v^{1/2}$. After linear fitting of the data, k_1 is calculated by the slope of the line and k_2 is obtained from the intercept of the line on y-axis. After knowing the values of k_1 and k_2 , the capacitive contribution of the current (non-diffusion-controlled current) and the current due to solid-state ion diffusion (i.e., diffusion-controlled current) can be calculated individually at all given potentials(V). This analysis is shown in figure S3. By linearly fitting the data, we have calculated the values of k_1 and k_2 at different potentials V.



Figure S3: Plots of $i/v^{1/2}$ and $v^{1/2}$ to calculate k_1 and k_2 values for pristine WS₂ electrode using eq. (5). Once the data is linearly fitted, the slope of the line gives k_1 value while the intercept on y axis gives k_2 value.

References

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