

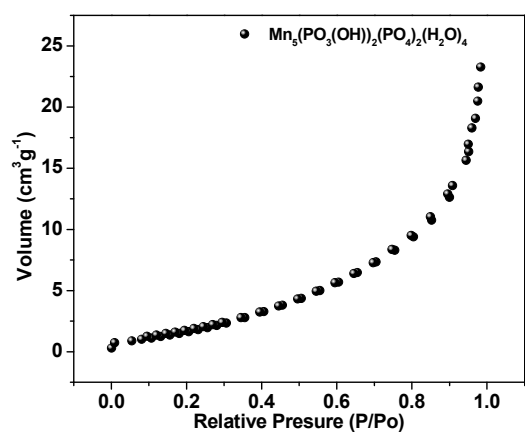


Figure S1. N₂ adsorption-desorption isotherm of Mn₅(H₂O)₄(PO₃OH)₂(PO₄)₂.

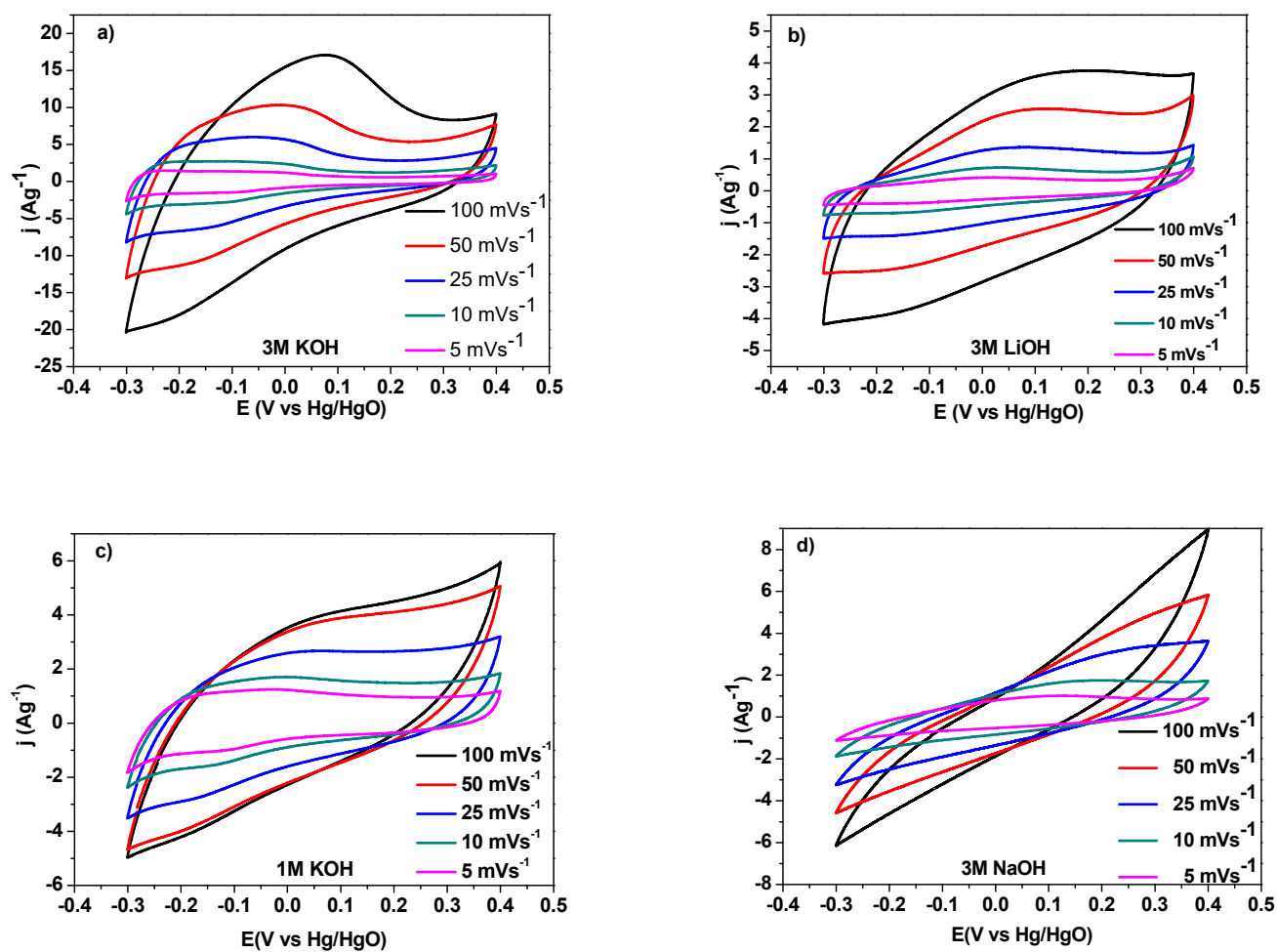


Figure S2. Cyclic voltammograms of Mn₅(H₂O)₄(PO₃OH)₂(PO₄)₂ up to 100 mVs⁻¹, in a) 3M KOH and b) 3M LiOH. In c) 1M KOH and d) 3M NaOH.

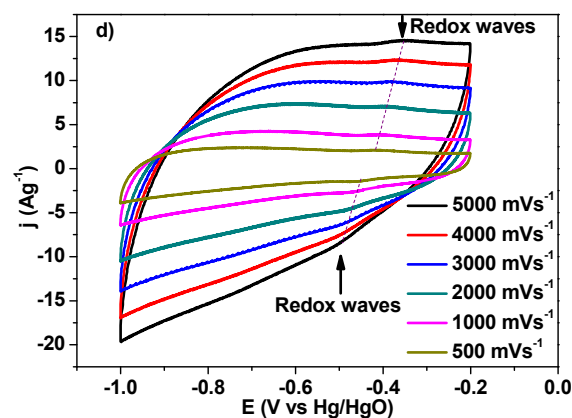
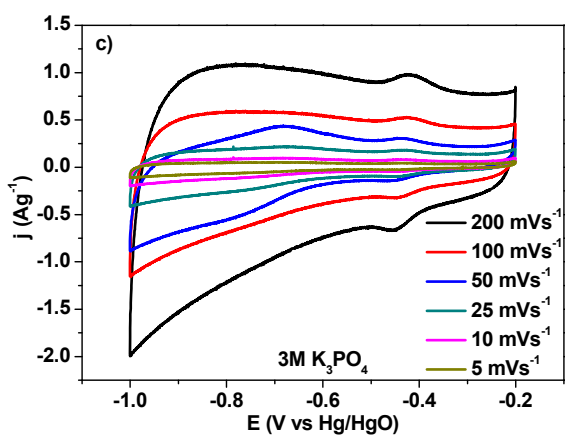
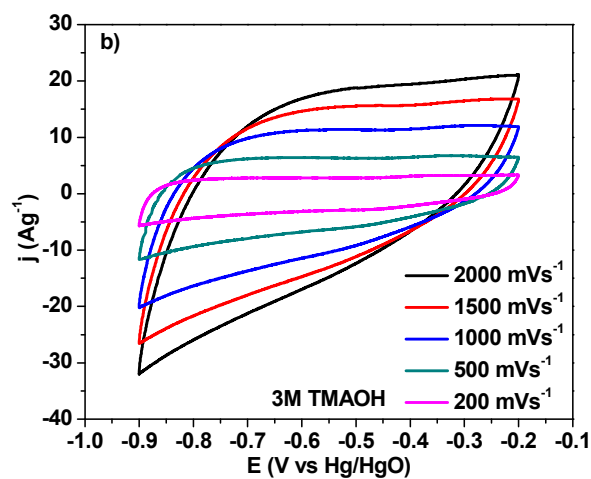
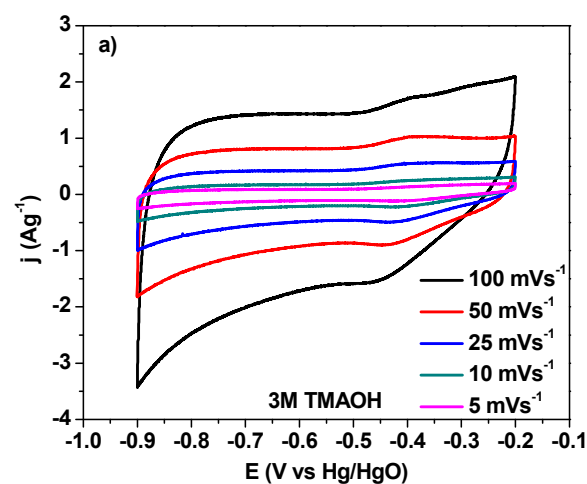
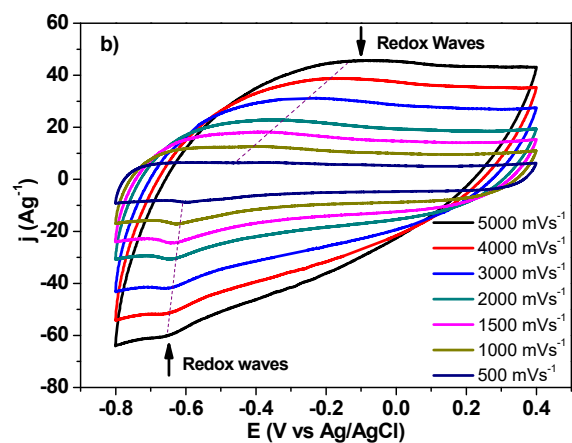
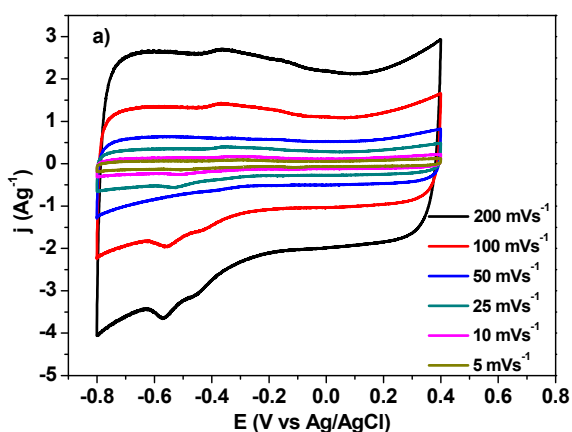


Figure S3. Cyclic voltammograms of $\text{Mn}_5(\text{H}_2\text{O})_4(\text{PO}_3\text{OH})_2(\text{PO}_4)_2$ in 3M TMAOH a) up to 100 mVs^{-1} and b) up to 2000 mVs^{-1} . In 3M K_3PO_4 c) up to 200 mVs^{-1} , and d) up to 5000 mVs^{-1} . The arrows and dashed lines are guides to the eye to highlight the redox waves at high scan rates.



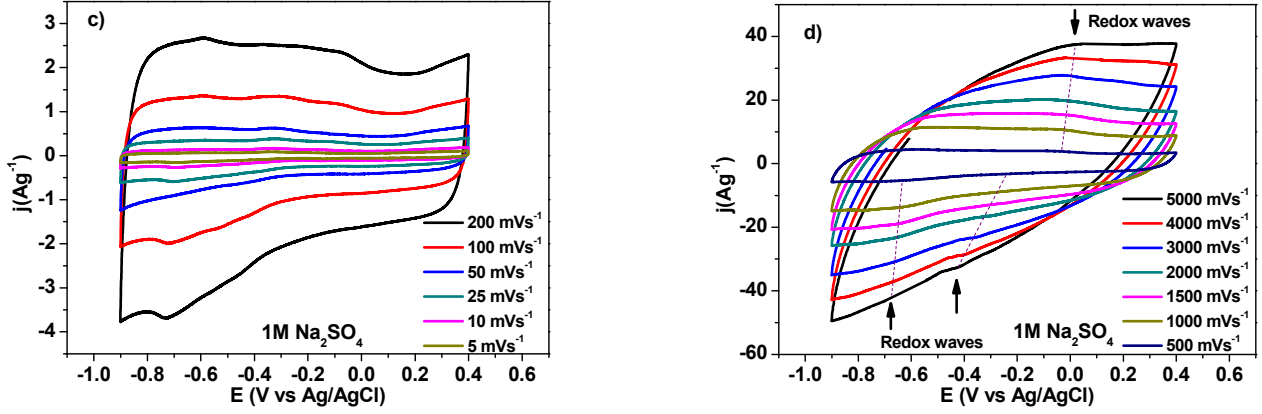


Figure S4. Cyclic voltammograms of $\text{Mn}_5(\text{H}_2\text{O})_4(\text{PO}_3\text{OH})_2(\text{PO}_4)_2$ in 5M LiNO_3 a) up to 200 mVs^{-1} , and b) up to 5000 mVs^{-1} . In $1\text{M Na}_2\text{SO}_4$ c) up to 200 mVs^{-1} and d) up to 5000 mVs^{-1} . The arrows and dashed lines are guides to the eye to highlight the redox waves at high scan rates.

The Trasatti-Dunn Coupled Method to Deconvolute the Charge in Cyclic Voltammograms.

The coupled method allows the deconvolution of cyclic voltammograms to determine the amount of charge that arise from the three known charge storage process in electrochemical capacitors, the electric double layer (EDL), pseudocapacitive and Faradaic processes.

In the Trasatti method [48], the total stored charge is considered as the contribution of the outer surface charge attributed to only the electric double layer and the inner charge that is attributed to both pseudocapacitive and Faradaic process (see equation 1).

$$q_T = q_o + q_i \quad (1)$$

q_o is the intercept of the linear plot of the voltametric charge $q(V)$, versus the sweep rate $v^{1/2}$, when $v \rightarrow \infty$ (see equation 2).

$$q(V) = q_o + C_1 v^{1/2} \quad (2)$$

Thus, the total charge, q_T is obtained from the intercept of the linear plot of $q(V)^{-1}$ versus $v^{1/2}$ when $v \rightarrow 0$ (see equation 3).

$$\frac{1}{q(V)} = \frac{1}{q_T} + C_2 v^{1/2} \quad (3)$$

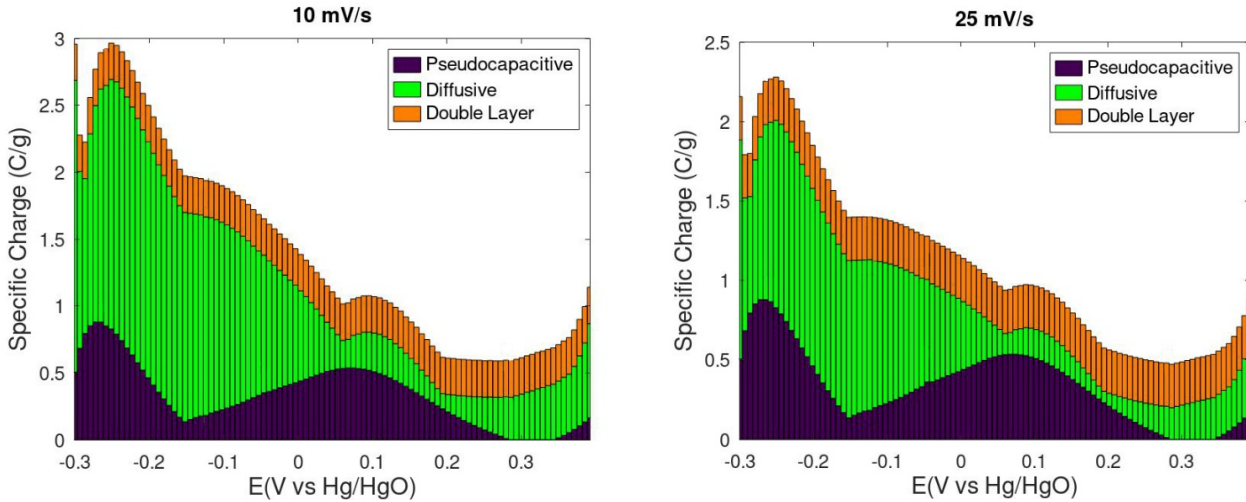
In this step, the method allows to estimate the outer charge. In other words, the charge that arise from the electric double layer process and the total charge, that includes the charge of pseudocapacitive processes and faradaic process. Thus, subtracting the double layer charge from the total charge leads to the inner charge that could be composed at least by one of the two processes, pseudocapacitive or faradaic.

Dunn method [49] allows to estimate the capacitive charge. This charge includes at least one of the following processes the electric double layer and pseudocapacitive process. The Dunn method also allows to estimate the charge that arises from diffusion-dependent processes like ion intercalation. The method is based on proportionality of the capacitive and pseudocapacitive current with v , the scan rate. The method also establishes that the diffusion, as the intercalation/deintercalation process is proportional to $v^{1/2}$ the square root of the scan rate. Thus, the total current is the contribution of the above processes (see equation 4). The rearrangement of equation 4 into equation 5 allows to estimate the two constants, k_1 from the slope and k_2 from the intercept of the plot $i(V)v^{-1/2}$ versus $v^{1/2}$ at each fixed potential. The origin of the current and thus the origin of the charge can be known at each potential step.

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

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

The deconvolution of the three charge storage processes can be achieved by subtracting the charge of the electric double layer estimated with the Trasatti method from the capacitive charge obtained with Dunn method (that includes EDL and pseudocapacitive charge). This leads to calculated values of the EDL, pseudocapacitive and faradaic charge [14,15].



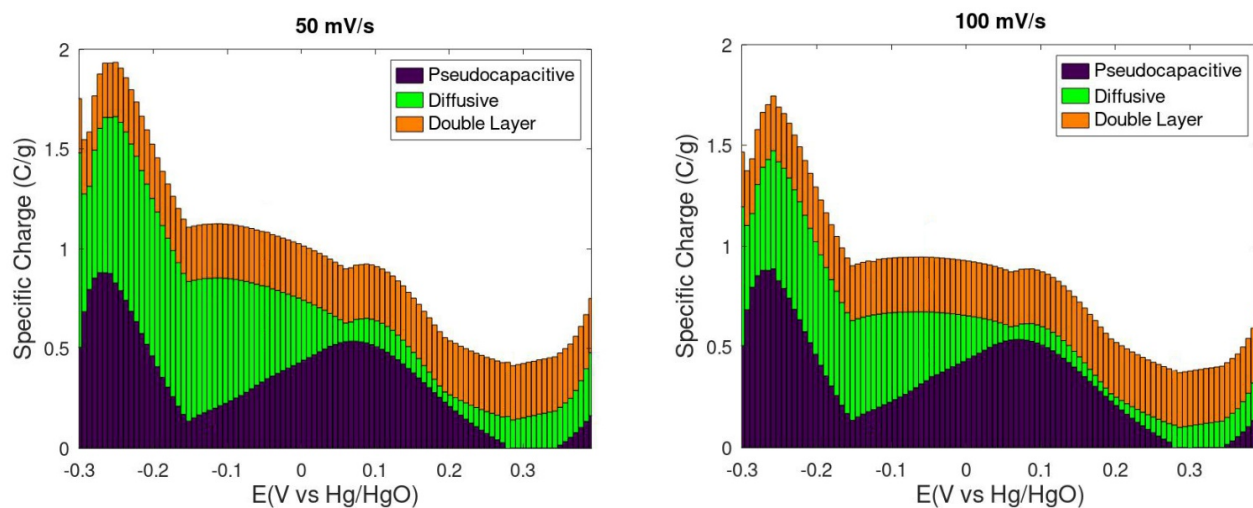


Figure S5. Specific charge as a function of applied potential at different scan rates in 3M KOH.

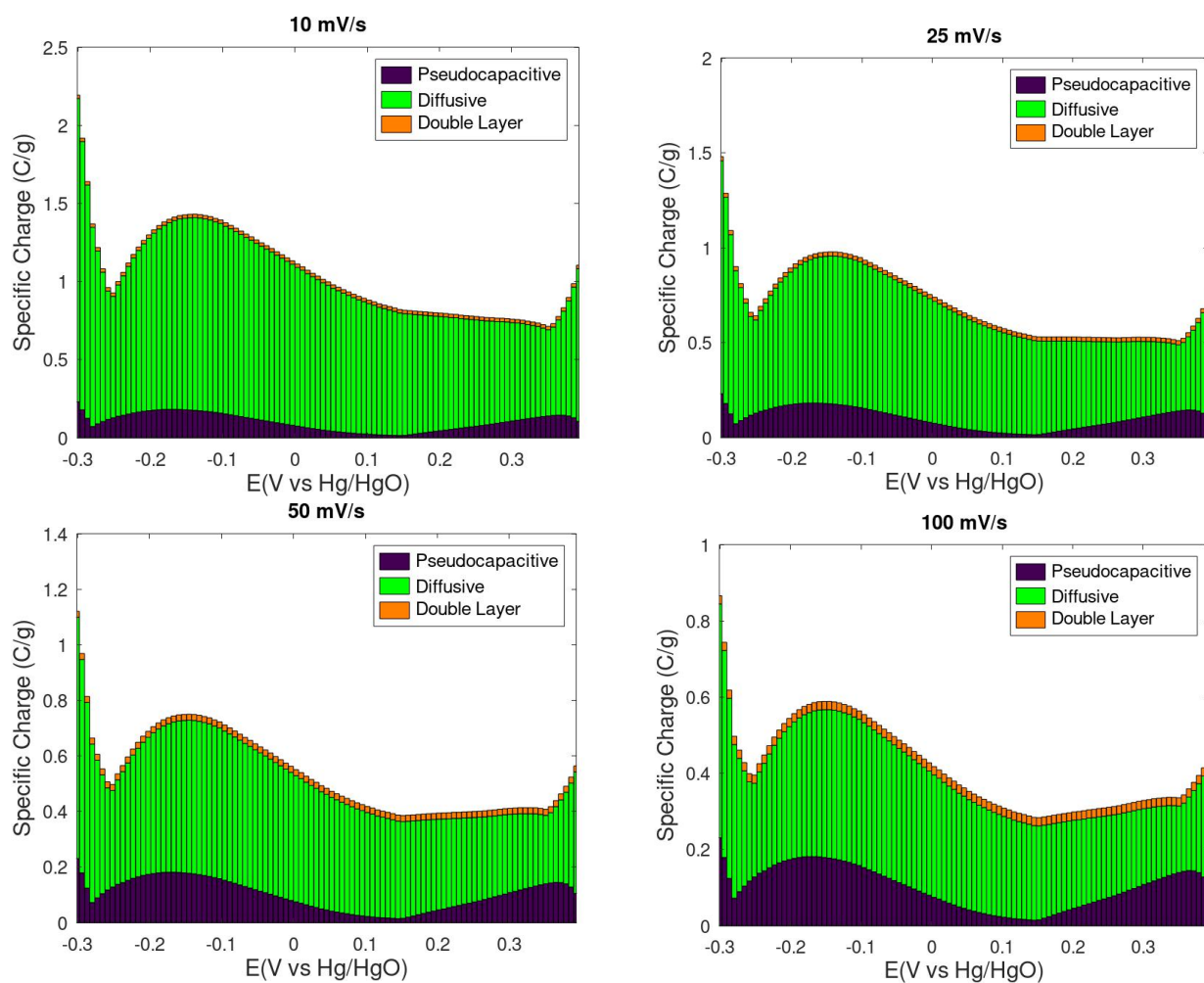


Figure S6. Specific charge as a function of applied potential at different scan rates in 1M KOH.

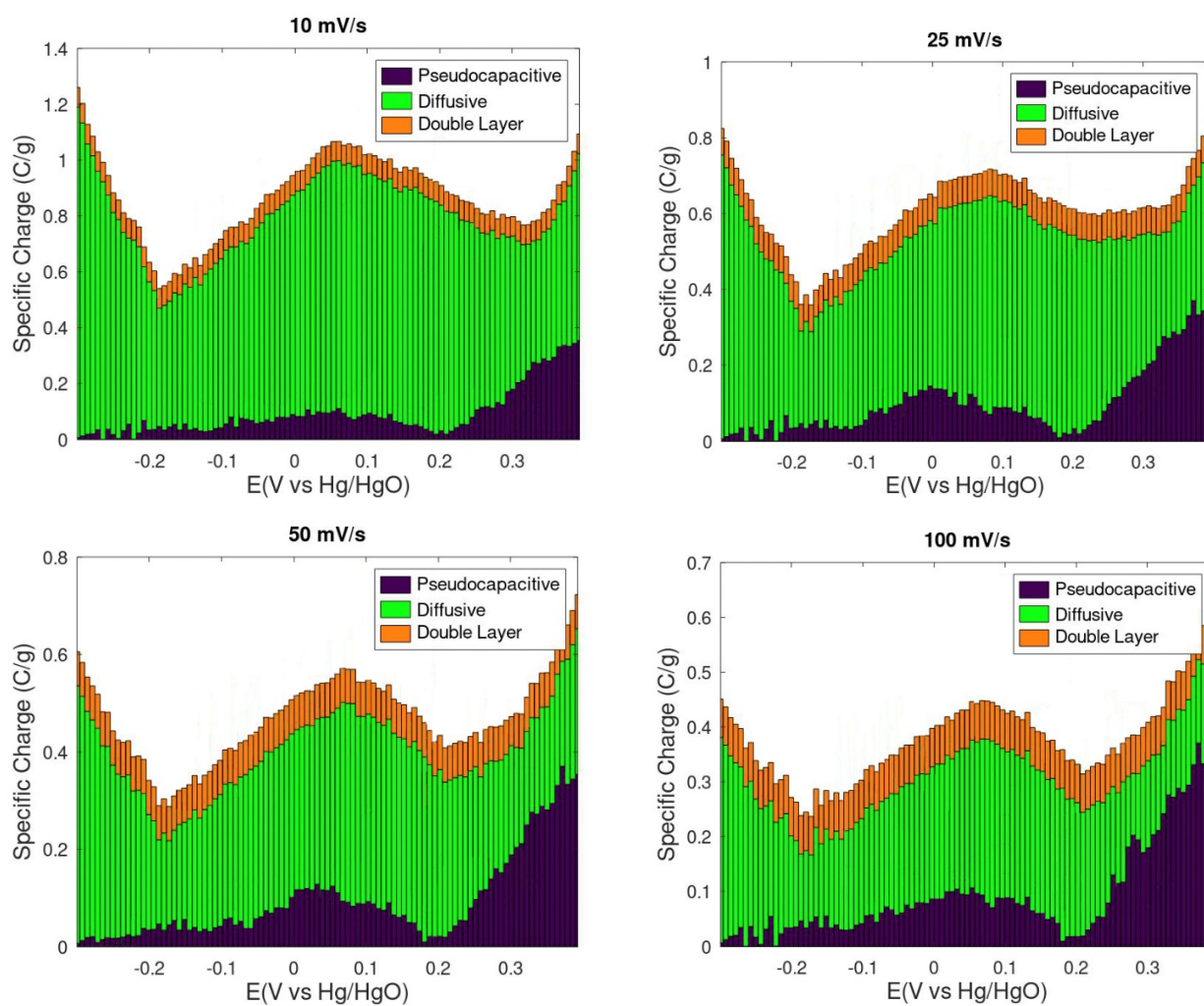
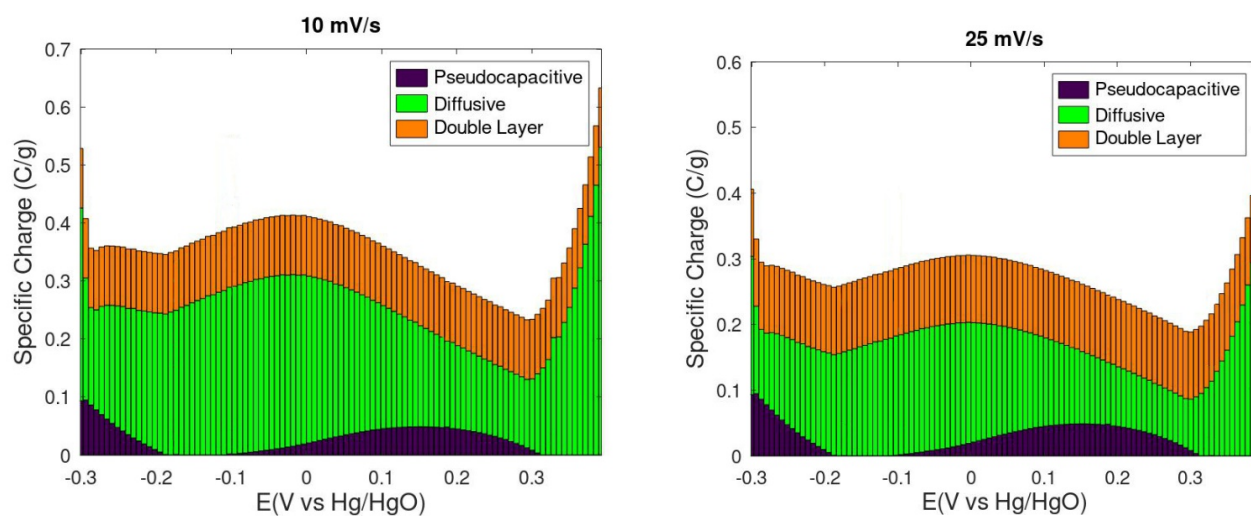


Figure S7. Specific charge as a function of applied potential at different scan rates in 3M NaOH.



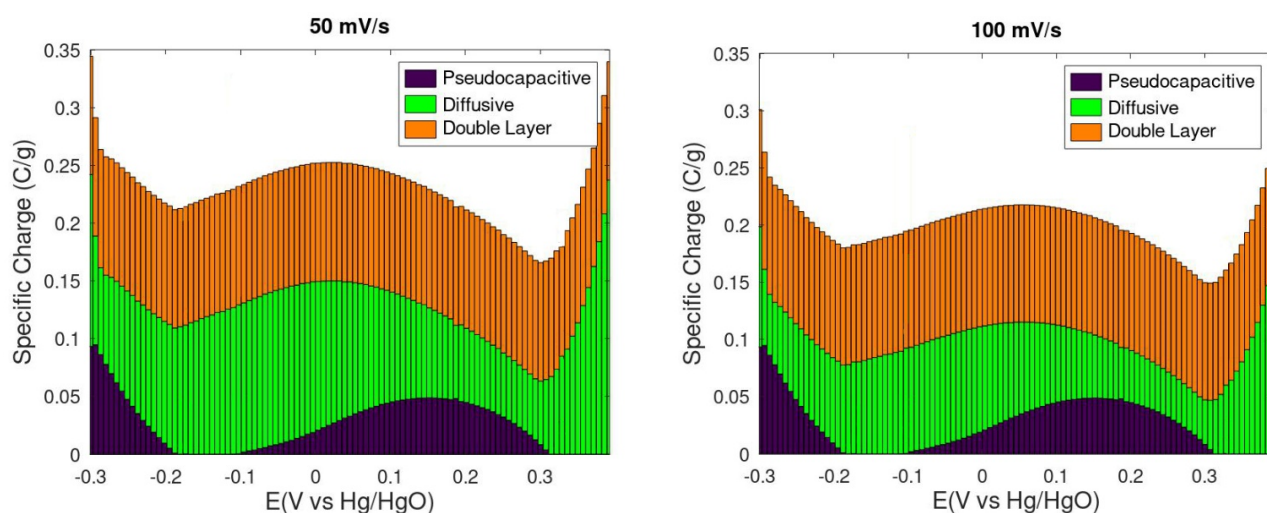


Figure S8. Specific charge as a function of applied potential at different scan rates in 3M LiOH.

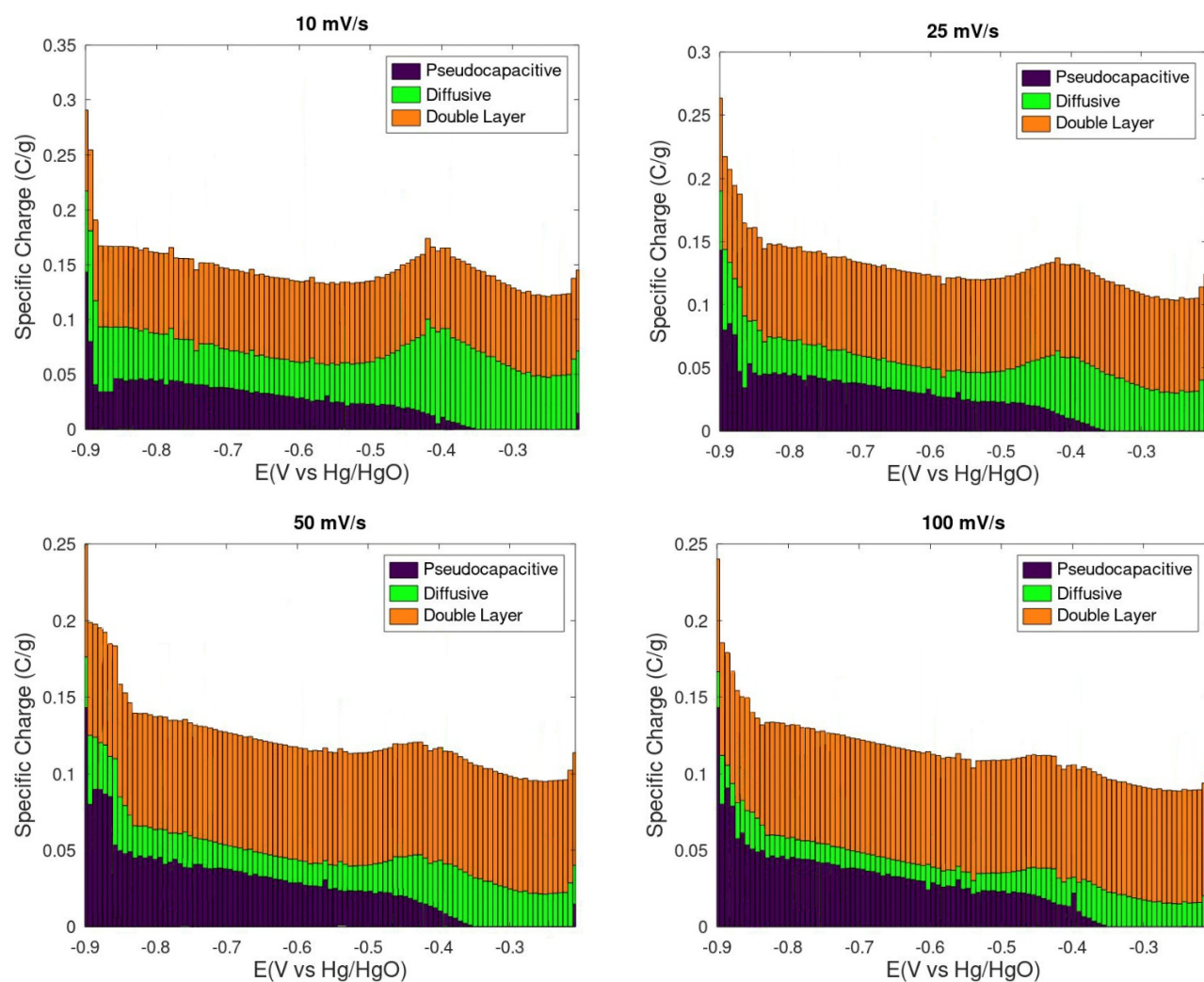


Figure S9. Specific charge as a function of applied potential at different scan rates in 3M TMAOH.

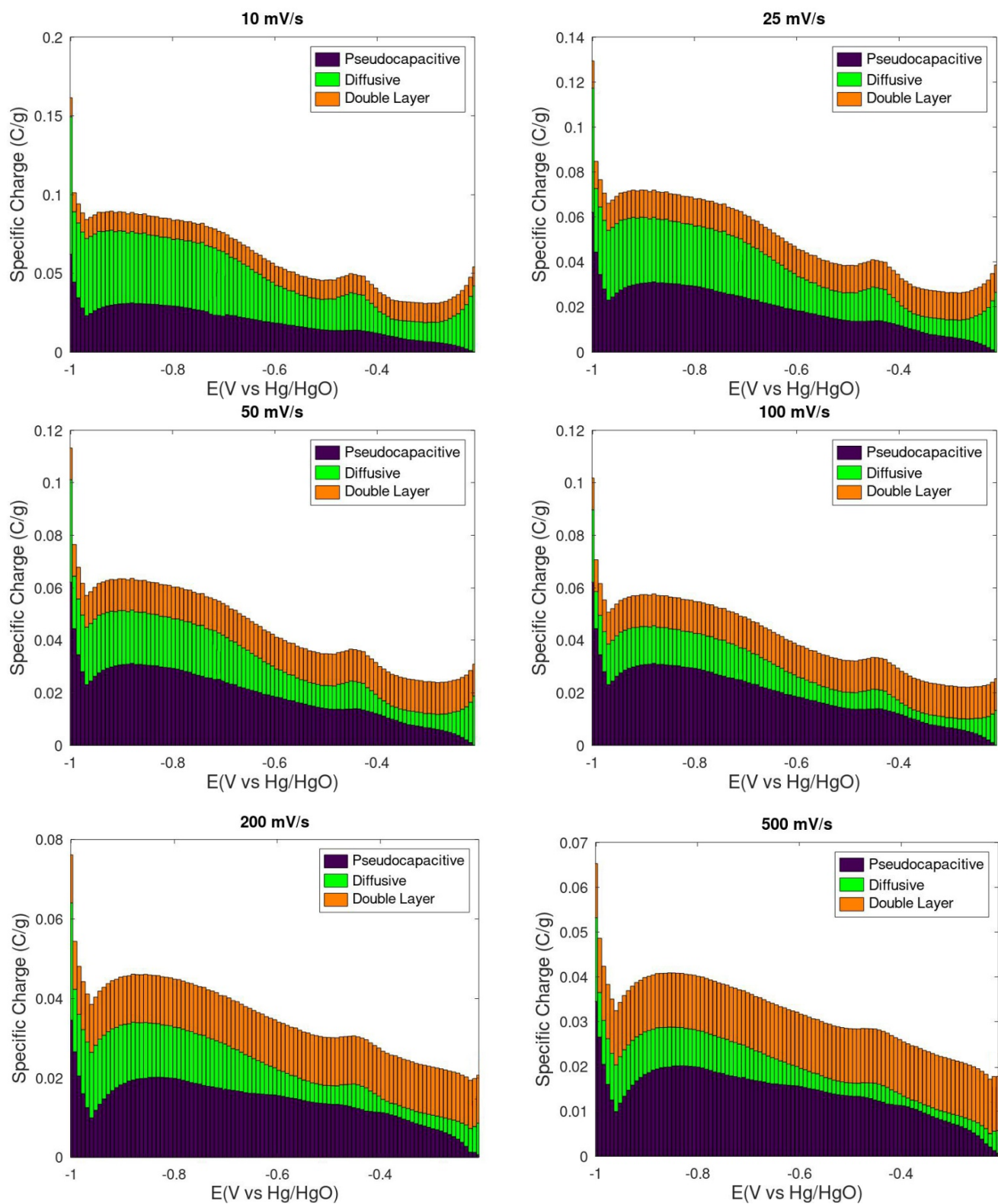


Figure S10. Specific charge as a function of applied potential at different scan rates in 3M K_3PO_4 .

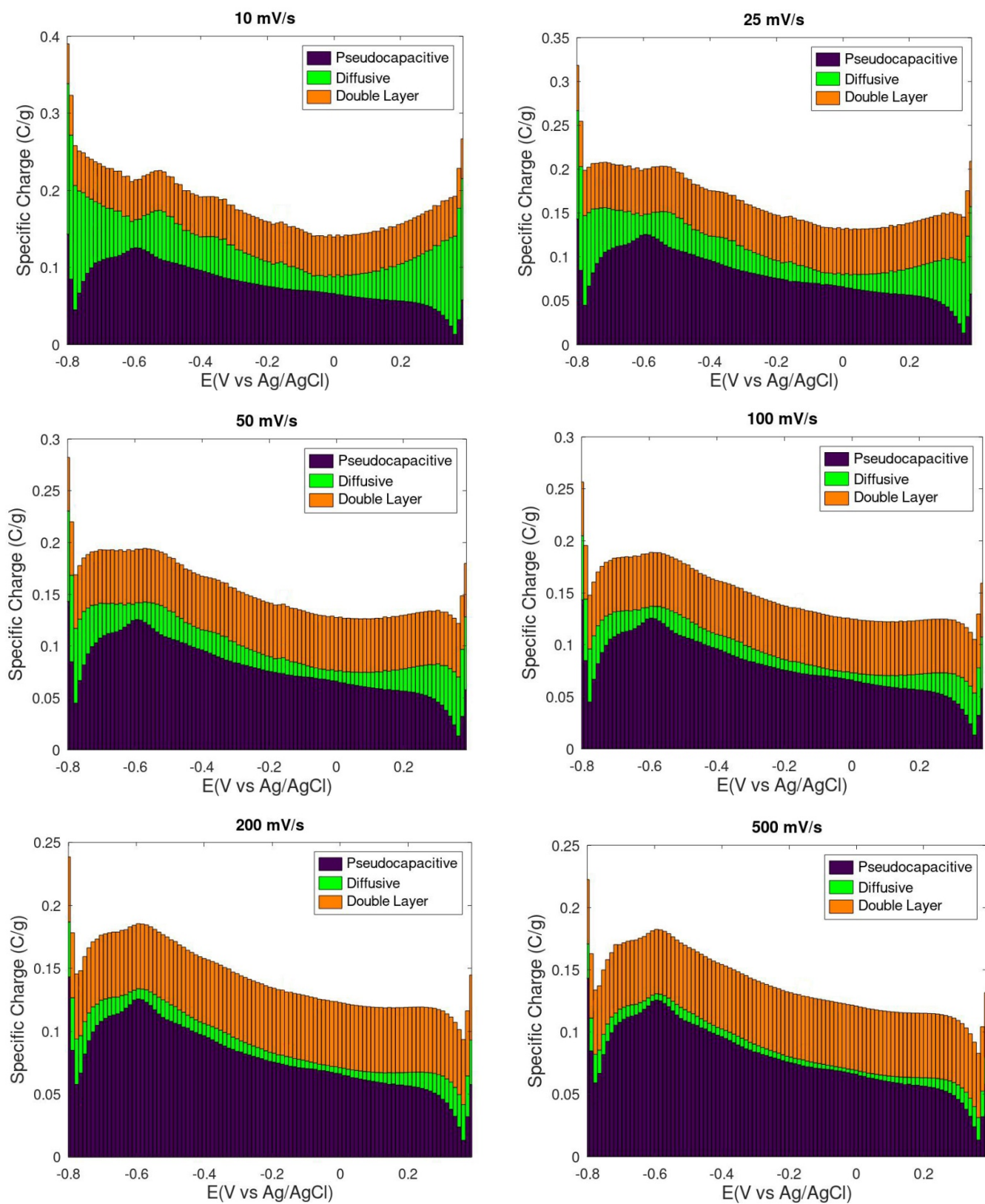


Figure S11. Specific charge as a function of applied potential at different scan rates in 5M LiNO₃.

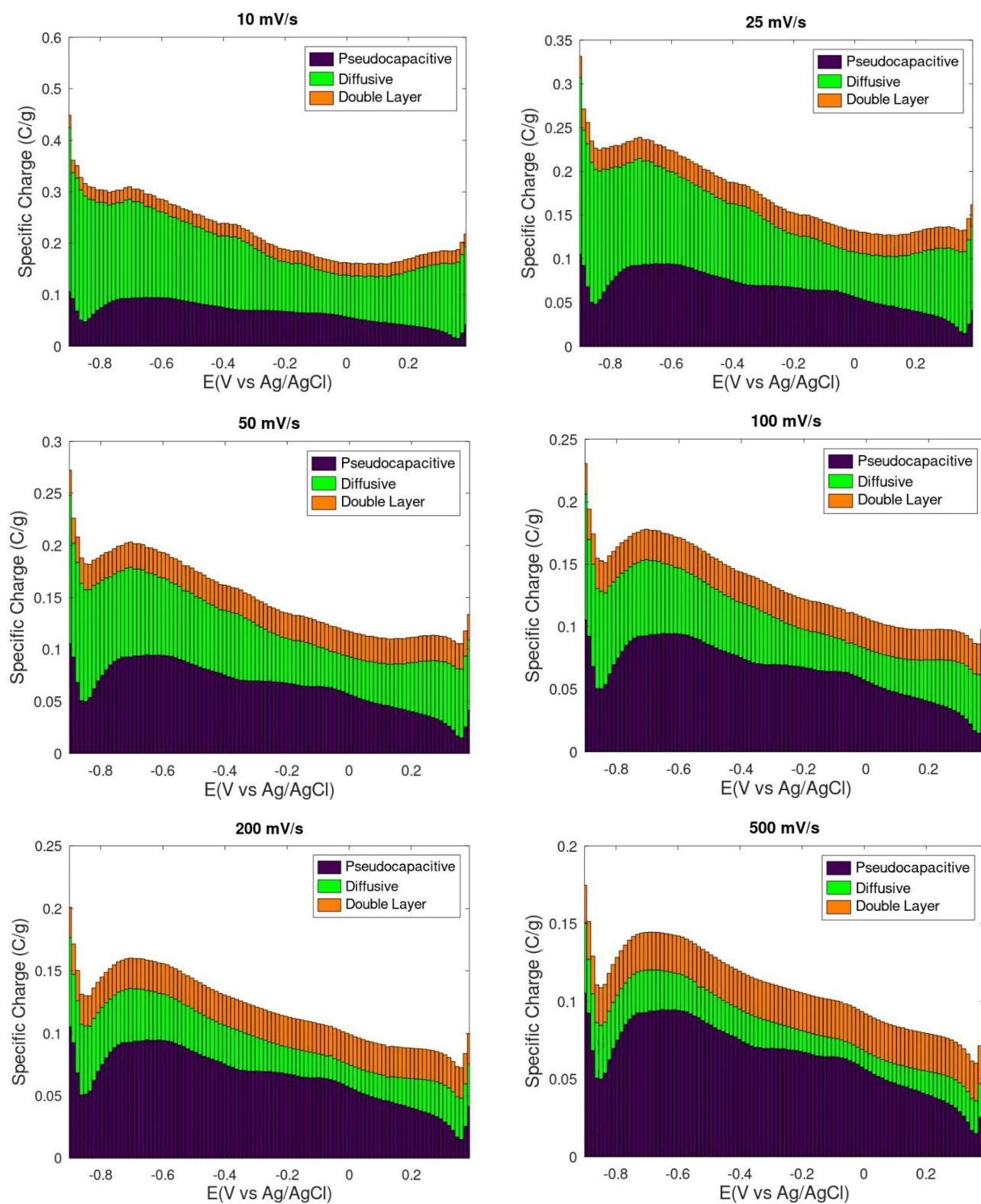


Figure S12. Specific charge as a function of applied potential at different scan rates in 1M Na₂SO₄.

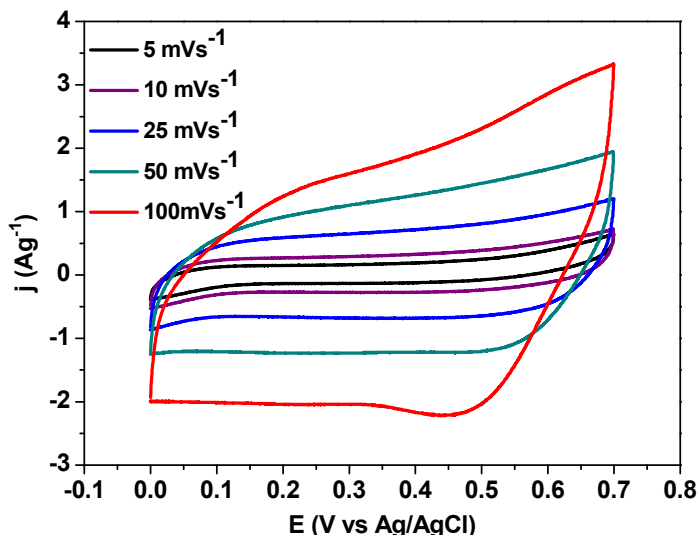


Figure S13. Cyclic voltammograms at different scan rate of $\text{Mn}_5(\text{H}_2\text{O})_4(\text{PO}_3\text{OH})_2(\text{PO}_4)_2$ Swagelok type device.

Active Thickness

The active thickness (how deep the ions move into the crystalline structure) is calculated with the equation 6, considering one-electron process.

$$\text{Active Thickness} = Q_D \cdot S^{-1} \cdot MM \cdot F^{-1} \cdot \rho^{-1} \quad (6)$$

Where “ Q_D ” is the diffusive charge in Cg^{-1} , “ S ” is the specific surface area of the active material in gcm^{-2} , “ MM ” the molecular weight in gmol^{-1} , “ F ” the Faraday constant and ρ the density of the active material in gcm^{-3} .

Areal Capacitance

The areal capacitance is calculated with the equation 7. Where C is the specific capacitance in Fg^{-1} , S the specific surface area in cm^2g^{-1} .

$$\text{Areal Capacitance } (\mu\text{Fcm}^{-2}) = C(\text{Fg}^{-1}) \cdot S^{-1}(\text{cm}^2\text{g}^{-1}) \cdot 10^6 \quad (7)$$

In order to compare the electrochemical performance between different materials with large difference on specific surface area, it is correct to report the areal capacitance. In this way, the intrinsic specific capacitance (that do not depend on specific surface area) is obtained and can be related to the crystalline structure, chemical composition, etc.

References

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15. J. Zúñiga, S. González, E. Le Calvez, R. Lucio Porto, I. Moreno, T. Brousse, L. López Pavón, J. Electrochem. Soc. 168, 090520, (2021).
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49. Torsten Brezesinski, John Wang, Julien Polleux, Bruce Dunn and Sara H. Tolbert. J. Am. Chem. Soc. 131, 1802-1809, (2009).