Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) is the most studied and explored mixed ion-electron conducting polymer system. PEDOT:PSS is commonly included as an electroactive conductor in various organic devices, e.g., supercapacitors, displays, transistors, and energy-converters. In spite of its long-term use as a material for storage and transport of charges, the fundamentals of its bulk capacitance remain poorly understood. Generally, charge storage in supercapacitors is due to formation of electrical double layers or redox reactions, and it is widely accepted that PEDOT:PSS belongs to the latter category. Herein, experimental evidence and theoretical modeling results are reported that significantly depart from this commonly accepted picture. By applying a two-phase, 2D modeling approach it is demonstrated that the major contribution to the capacitance of the two-phase PEDOT:PSS originates from electrical double layers formed along the interfaces between nanoscaled PEDOT-rich and PSS-rich interconnected grains that comprises two phases of the bulk of PEDOT:PSS. This new insight paves a way for designing materials and devices, based on mixed ion-electron conductors, with improved performance.