High performance Si/polyacrylonitrile (PAN) composite negative electrodes are fabricated by a robust process of heat treatment in air at a temperature between 250 and 400^{o}C. With a Si mass loading of 1 mg/cm^{2}, a discharge capacity of 1614 mAh/g at the 100th cycle is observed from the 400^{o}C treated Si/PAN composite electrode when cycled at a rate of C/3. Multiple techniques, including XRD, SEM, EDX, TGA, XPS, EIS, Raman, TEM, and nanoindentation, are employed to investigate the structural, chemical, and mechanical properties of the Si/PAN composite electrodes before and after heat treatment. Results show that the cyclization of PAN occurs at 250^{o}C. With increasing temperature, oxidation, dehydration, aromatization, and intermolecular crosslinking take place in PAN, resulting in a stable cyclized structure which functions as both a binder and a conductive agent in the Si/PAN composite electrodes. Meanwhile, PAN reacts with oxygen, forming volatile products and producing progressively porous Si/PAN composites with increasing temperature. This facile method of synthesizing Si-based composite negative electrodes can potentially be applied to other Si/polymer systems for further increasing the power/energy density of lithium ion batteries.