第 23 卷第 6 期
2008 年 11 月

热 能 动 力 工 程
JOURNAL OF ENGINEERING FOR THERMAL ENERGY AND POWER

Vol. 23, No. 6
Nov., 2008

文章编号: 1001—2060(2008)06—0682—03

成型前后活性炭储氢性能的初步研究

郑青榕[1], 顾安忠[2], 蔡振雄[1], 陈 武[1]

(1. 集美大学 轮机工程学院, 福建 厦门 361021; 2. 上海交通大学 制冷与低温工程研究所, 上海 200030)

摘 要: 初步分析成型措施对活性炭储氢特性的影响。首先, 在温度区间 113~293 K、压力范围 0~12.5 MPa 测定氢平衡吸附数据, 比较氢在未成型和经丙烯酸甲脂乳胶粘合剂成型的 YK—1 活性炭上的吸附量和等量吸附热; 其次, 通过储罐在室温、10.5 MPa 压力下的快速充/放气试验, 分析成型措施对储罐吸附床吸附热效应的影响。结果表明, 成型措施改变活性炭的密度和比表面积, 使吸附量和吸附床中心在充放气过程的温度曲线以及吸附床的脱氢流率发生变化; 在活性炭成型后, 必须强化吸附床传热或引入吸附热管理措施以抑制吸附过程热效应。

关 键 词: 氢气; 吸附; 充气; 放气; 成型活性炭

中图分类号: TK91 文献标识码: A

引 言

自20世纪60年代以来, 碳基材料低温吸附储氢就受到关注[1~3]。如天然气的吸附储存, 吸附储氢也面临吸附剂成型及吸附热效应管理等问题[4~6]。由于碳基材料的导热性能较差, 吸附热使充放气过程为非等温过程, 而使充气量小于等温充气过程的充气量; 在放气过程中, 又使部分气体无法脱附, 减小了储存容量甚至可能破坏吸附剂结构。此外, 成型措施会改变材料的微孔结构和比表面积、增大单位体积产热量, 由此加剧吸附热效应。因此, 有必要展开成型活性炭吸附床储放氢特性的研究。

本文选用热固型丙烯酸甲脂乳胶粘合剂对上海活性炭厂有限公司生产的椰壳活性炭 YK-1 成型处理, 在温度区间 113~293 K、压力范围 0~12.5 MPa, 测定氢在成型前后活性炭上的吸附等温线; 在室温、10.5 MPa 压力下, 对活性炭吸附床进行快速充放气试验, 从吸附床中心温度和吸附床脱氢流率的变化中分析成型措施的影响。

1 平衡吸附量测试

1.1 吸附等温线

成型时先将粘合剂和水混合, 然后按一定比例将混合物倒入盛有活性炭的容器内, 混合均匀后放入与试验容器相匹配的模具内由压力机压制成型, 成型前后活性炭的主要数据如表 1 所示。从表中可看出, 活性炭与粘合剂的比例为 1∶0.2 时, 活性炭密度增大但其比表面积减小较少。由于氢吸附处于超临界温度区域, 吸附剂的比表面积和微孔容积为影响储氢性能的关键因素, 本文选用比例为 1∶0.2 时的成型活性炭 FC-2 作对比分析。

表 1 YK—1 活性炭成型前后的结构参数

样品	质量比	密度/$kg \cdot L^{-1}$	BET 比表面积/$m^2 \cdot g^{-1}$
YK-1	1:0	0.453	1 200
FC-1	1:0.1	0.512	1 120
FC-2	1:0.2	0.567	1 042
FC-3	1:0.3	0.614	896

采用容积法测试吸附等温线, 测试原理及步骤见文献[7]。在温度区间 113~293 K、压力范围 0~12.5 MPa 测得的氢吸附等温线如图 1 所示。从图中可以发现, 成型活性炭的吸附量略有减小, 但等温线形状与未成型前的相似。

1.2 等量吸附热

等量吸附热 q_{st} 可表示为[8]:

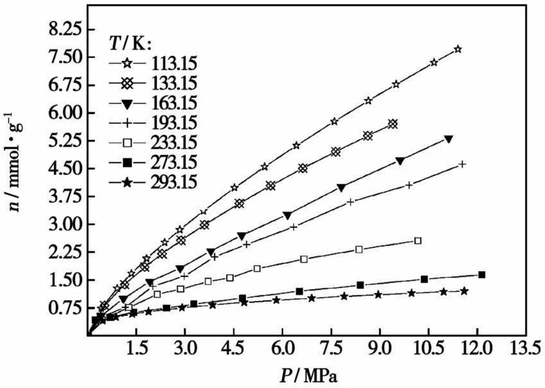
$$q_{st} = -\Delta H = -R\left[\frac{d\ln f}{d(1/T)}\right]_n \qquad (1)$$

式中: f—与平衡压力对应的逸度, Pa; H—焓, J/mol; R—通用气体常数, J/(mol·K); T—温度, K; n—单位质量吸附剂上的吸附量, mmol/g。在试验范围内选择 4 个吸附量作 $\ln f$ 对 T^{-1} 的标绘, 结果如图 2 所示, 表 2 为式(1)的计算结果, 从中可得出氢在成型和未成型活性炭上的平均等量吸附热分别为 4.53 和 4.48 kJ/mol。表明成型措施对吸附剂结构及堆积密度的影响较小, 等量吸附热的数值变化不大。

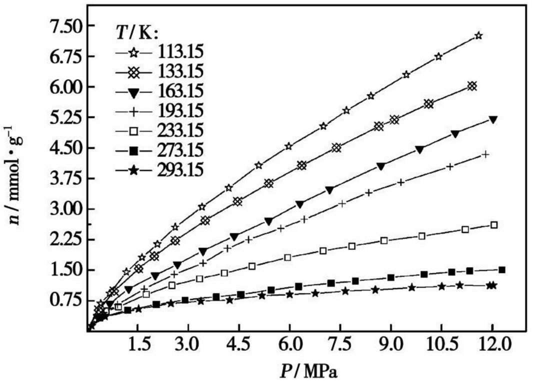
收稿日期: 2007—09—11; 修订日期: 2007—12—31

基金项目: 福建省青年人才创新基金资助项目(2006F3092); 福建省自然科学基金资助项目(E0640016)

作者简介: 郑青榕(1967—), 男, 福建永定人, 集美大学副教授, 博士后.

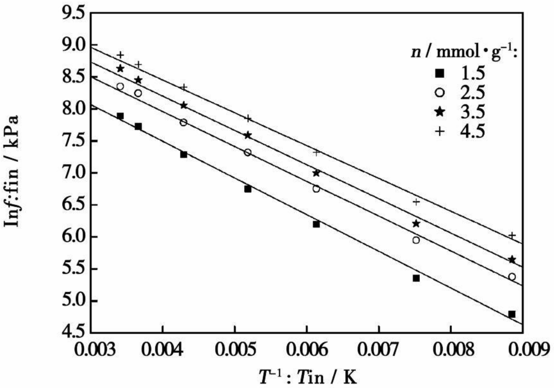


(a) 成型前

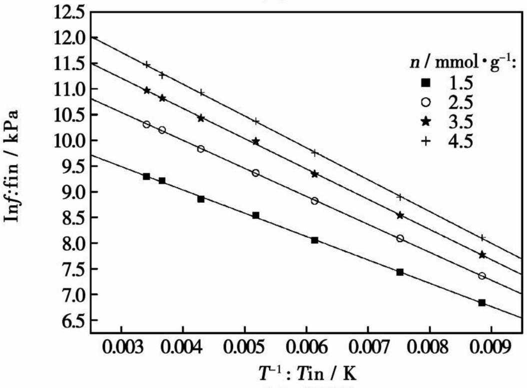


(b) 成型后

图 1　氢在成型前后活性炭 YK-1 上的吸附等温线



(a) 成型前



(b) 成型后

图 2　氢在成型前后活性炭 YK-1 上的等量吸附线标绘

表 2　氢在成型前后 YK-1 活性炭上的等量吸附热

n/mmol◦g^{-1}	成型活性炭 q_{st}/J◦mol^{-1}	未成型活性炭 q_{st}/J◦mol^{-1}
1.5	5 145.67	4 763.86
2.5	4 894.05	4 527.17
3.5	4 523.33	4 442.40
4.5	3 771.89	4 260.01

2　充放气试验

试验吸附容器的结构及测温热电偶布置如图 3 所示, 5 号热电偶测点位于储罐中部的中心, 试验步骤参见文献[4~5]。

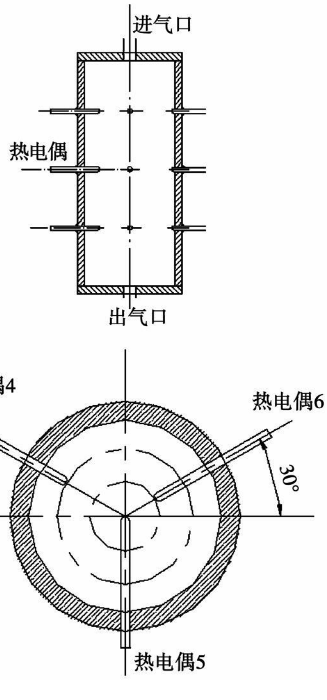


图 3　吸附容器结构及热电偶布置示意图

2.1　充气试验

图 4 显示活性炭吸附床中心在 10.5 MPa 压力下快速充气过程中的温度变化。从图中可看出, 由于单位体积储氢密度增大, 更多氢气分子进入增加了分子间相互压缩做功的产热, 加剧了吸附过程热效应, 吸附床中心在充气过程中的最大温升从未成型时的 35 ℃上升至 45 ℃。

从图 4 中还可发现, 成型措施将使活性炭吸附床中心到达最高温度的时间推迟近 100 s, 温度曲线在整个充气过程中的变化也较为平缓。这表明, 活性炭成型后体积储氢密度增大, 但未改善吸附床的传热性能, 较大数量的吸附热和压缩气体产热使吸附床处于较高的温度。

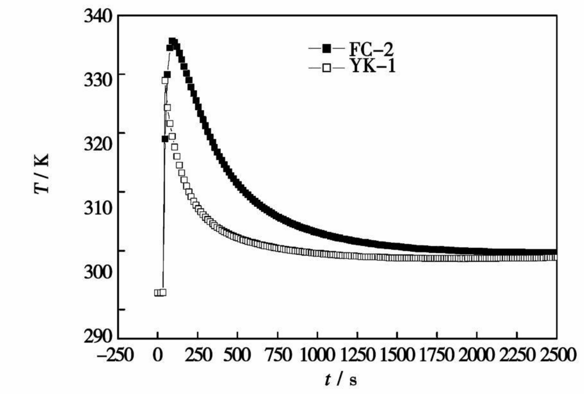
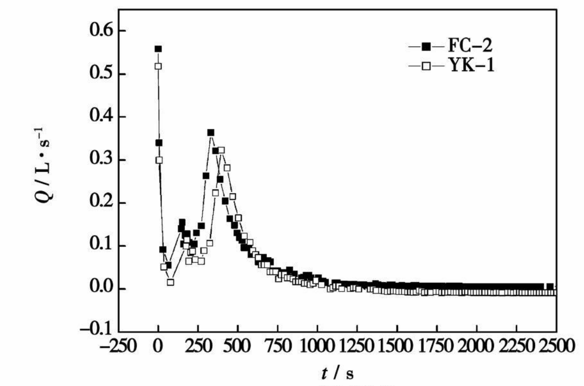
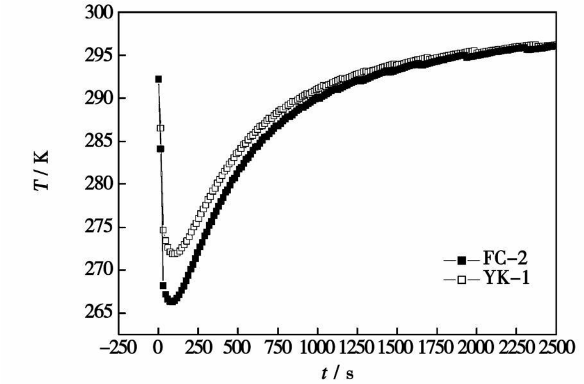


图4　储罐中心在压力为10.5 MPa下快速充气过程的温度变化

2.2　放气试验



(a) 脱气流率



(b) 曲线温度

图5　吸附床中心在储罐压力为10.5 MPa下快速放气时的脱气流率及温度曲线

图5反映了活性炭吸附床在10.5 MPa压力下快速放气时的放气流率Q和吸附床中心温度的变化情况。从图5(a)中可看出，成型措施虽然减小了吸附剂的比表面积，但未改变吸附床的脱附特性，相反由于单位体积储氢密度的增大，吸附床的放气流率Q将增大。此外，从图5(b)中还可发现，由于吸附床的传热性能未改善，吸附床中心在快速放气过程中的最大温降也降低了近10 ℃。

比较图5(a)和(b)的横坐标可发现，吸附床中心温度在脱气后的120 s左右降至最低值，脱气流率Q也同时降至最小，然后随着吸附床温度回升，吸附床持续脱附氢直到800 s左右(Q降为0.02 L/s)，此时储存氢大部分已脱附。因此，可采取强化传热措施抑制吸附床在脱附初始阶段的温度波动以加快脱附进程。

3　结　语

(1) 选用合适的混合比例，热固型丙烯酸甲脂乳胶粘合剂可提高活性炭的体积储氢密度。但由于YK-1活性炭的密度较高、比表面积较小，成型措施未能显著影响氢平衡吸附量和等量吸附热。

(2) 热固型丙烯酸甲脂乳胶粘合剂的导热性能较差，成型后活性炭吸附床的导热性能并没有改善，使得吸附床在充放气过程中的温度波动加剧，影响了吸附床的吸脱氢性能，必须采取措施抑制吸附床在初始充放气阶段的温度波动以改善吸附床的储氢性能。

(3) 后续工作应选择较大比表面积和较低密度的活性炭，从优选粘合剂、强化吸附床传热和有效管理吸附热3方面，结合更多工况下的试验和吸附床的数值模拟中展开研究。

参考文献：

[1] KIDNAY A, HIZA M. High pressure adsorption isotherm of neon, hydrogen and helium at 76 K[J]. Advances in Cryogenic Engineering, 1967, 12: 730.

[2] STRÖBEL R, GARCHE J, MOSELEY P T, et al. Hydrogen storage by carbon materials[J]. Journal of Power Sources, 2006, 159(2): 781— 801.

[3] BÉNARD P, CHAHINE R. Storage of hydrogen by physisorption on carbon and nanostructured materials[J]. Scripta Materialia, 2007, 56(10): 803— 808.

[4] YANG X D, ZHENG Q R, GU A Z, et al. Experimental studies of the performance of adsorbed natural gas storage system during discharge[J]. Applied Thermal Engineering, 2005, 25(4): 591— 601.

[5] 郑青榕，顾安忠，蔡振雄，等. 活性炭吸附储氢罐充放气过程的试验研究[J]. 武汉理工大学学报，2006, 28(专辑Ⅱ): 374— 379.

[6] HERMOSILLA LARA G, MOMEN G, MARTY P H, et al. Hydrogen storage by adsorption on activated carbon: investigation of the thermal effects during the charging process[J]. International Journal of Hydrogen Energy, 2007, 32(10—11): 1542— 1553.

[7] 郑青榕. 多壁碳纳米管吸附储氢研究[D]. 上海：上海交通大学，2002.

[8] NICHOLSON D, PARSONAGE N G. Computer simulation and the statistical mechanics of adsorption[M]. London: Academic Press, 1982.

(编辑　单丽华)

The authors have analyzed the working principle of a hydraulic torque converter used for a wind power generation system to realize speed variation and constant frequency. To secure maximal wind power with a comprehensive consideration of the structural parameters of a mechanical transmission system, determined was the output speed regulation range of the hydraulic torque converter, capable of accommodating to any change of wind-wheel rotating speed and keeping a generator operating at a constant speed. On the basis of the torque balancing relationship of the transmission system and in conjunction with the torque-speed characteristics of a windmill rotor, the input power of a pump wheel has been calculated. Herefrom, the characteristic geometric parameters of the hydraulic torque converter was tentatively ascertained. From an energy balance equation, the efficiency of the whole transmission system was evaluated. The above research has laid a theoretical and analytic basis for the popularization of hydraulic transmission in wind power generation systems. **Key words**: wind power generation, transmission system, hydraulic torque converter

200 MW 锅炉空气分级低 NO_x 燃烧改造实验研究= **Experimental Study of an Air-staged and Low NO_x Emission-based Combustion Modification to a 200 MW Boiler**[刊，汉] /ZHANG Xiao-hui, SUN Rui, SUN Shao-zeng, et al (College of Energy Science and Engineering, Harbin Institute of Technology, Harbin, China, Post Code: 150001)//Journal of Engineering for Thermal Energy & Power.— 2008, 23(6).—676～681

To reconstruct the combustion system of a 200 MW bitumite-fired boiler in a power plant in Beijing region for reducing NO_x emissions, a cubic-staged low-NO_x emission combustion system combining overfired air (OFA) with low-NO_x emission burners of horizontal bias-combustion was used. After the modification, the NO_x emissions concentration has been improved conspicuously. The above-mentioned concentration can be reduced by 45% to 60% when an equalization air distribution mode was adopted. The use of a proper horizontal swinging angle for the OFA nozzle will effectively lessen the flue gas temperature deviation at the furnace outlet, which can be controlled within a range of 50 ℃. In addition to a marked lowering of NO_x emissions, the boiler efficiency can be enhanced by about 1%. After the modification, the NO_x emissions concentration at any operating condition is all below 400 mg/m^3 and in the meantime, this can provide more favorable inlet conditions for tail portion flue-gas SCR (Selective Catalyst Reduction) device. **Key words**: coal-fired boiler, staged combustion technology, overfired air (OFA), horizontal bias combustion and low-NO_x emission burner, NO_x emission concentration

成型前后活性炭储氢性能的初步研究= **A Preliminary Study of the Hydrogen Storage Performance of Activated Carbon Before and After its Shape-formation**[刊，汉] /ZHENG Qing-rong, CAI Zhen-xiong, CHEN Wu (College of Marine Engineering, Jimei University, Xiamen, China, Post Code: 361021), GU An-zhong (Research Institute of Refrigeration and Cryogenic Engineering, Shanghai Jiaotong University, Shanghai, China, Post Code: 200030)//Journal of Engineering for Thermal Energy & Power.— 2008, 23(6).—682～684

The influence of shape-formation measures on the hydrogen storage characteristics of activated carbon was preliminarily analyzed. First, hydrogen equilibrium adsorption data were determined in a temperature range from 113 to 293 K and at a pressure range from 0 to 12.5 MPa. The adsorptive quantity and equivalent adsorptive heat of hydrogen on activated carbon YK-1 were compared in two cases: i. e. 1. when hydrogen has not undergone a shape formation; and 2. it has completed such a formation by use of acrylate methyl ester emulsion adhesive. Secondly, through a quick inflation and deflation test of a storage tank at a room temperature and a 10.5 MPa pressure, the influence of the shape-formation measures on the adsorptive thermal effect of a storage-tank adsorptive bed was analyzed. It has been found that the shape-formation measures can change the density and specific surface area of the activated carbon, causing a change of the adsorptive quantity and temperature curve of the adsorptive bed center during the inflation and deflation process as well as a change of dehydrogenation flow rate of the adsorptive bed. After the activated carbon has taken shape, the heat transfer through the adsorptive bed must be intensified, or adsorptive heat management measures, introduced to suppress the thermal effect of the adsorptive process. **Key words**: hydrogen, adsorption, inflation, deflation, shape-formed activated carbon