

用于海工结构阴极保护系统的水泥基阳极材料制备与性能

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摘 要: 外加电场阴极保护(ICCP)是保障海洋环境钢筋混凝土结构耐久性和服役寿命的重要途径, 但存在常规金属阳极材料消耗量大等问题, 因此提出研制兼具优异力学性能和导电性能的水泥基阳极材料。实验室制备了 2 种水泥基阳极材料, 兼具表面防护和导电阳极功能, 分别为内掺碳纤维、碳纳米纤维的高强导电砂浆材料和内嵌碳纤维网格布的导电砂浆材料; 分别对 2 种阳极材料进行了力学性能、电阻率、抗渗性测试, 并研究了在 ICCP 加速电场作用下的性能演变规律。结果表明: 2 种阳极材料均具有优异的力学性能, 其抗压、抗弯强度分别最达 103.0 MPa 与 14.6 MPa; 导电性能良好, 电阻率最低为 160 $\Omega \cdot \text{cm}$; 气体渗透率和毛细吸水速率仅为普通混凝土的 1/10, 对混凝土结构具有良好的物理防护效果。ICCP 加速试验后, 2 种材料的力学性能、导电性能仅产生轻微劣化现象, 其中引入碳纤维网格布的阳极材料性能更加稳定, 适用于重点混凝土工程的外加电流阴极保护, 也可用于高氯盐环境条件下的混凝土构件电化学除氯, 可望替代传统阳极材料。

关键词: 海工混凝土; 阴极保护; 水泥基阳极材料; 力学性能; 导电性能; 抗渗性

中图分类号: TU528 **文献标志码:** A **文章编号:** 0454-5648(2024)02-0485-13

网络出版时间: 2023-12-06



近年来, 中国加快“海洋强国”的脚步, 由此在海洋工程建设过程中开发新型先进海洋材料具有非常重大的意义。在海洋环境中, 钢筋混凝土构件极易受到海水中有毒离子的腐蚀而发生严重破坏^[1-3]。钢筋混凝土构件防腐方法有: 对混凝土及钢筋进行涂层处理、选择超高性能混凝土作为构件基体、添加化学外加剂如腐蚀抑制剂、电化学除氯、以及进行外加电流阴极保护方法(ICCP)等^[4-8]。而 ICCP 也被证实是钢筋混凝土结构保护的优秀方法^[9-11], 其电流可控, 可适用于高阻环境、对混凝土影响小且可长期使用^[12]。ICCP 方法为钢筋混凝土构件提供外加电流, 从而保护构件长期不被腐蚀。此外, 对于已发生腐蚀的构件, ICCP 方法可以实现氯离子向外迁移, 保证构件其他完好部分不再受侵蚀。

ICCP 保护系统分为 3 个部分, 分别为阴极、外部阳极以及电源^[13], 对于海洋工程防腐, 制备出高性能的阳极材料是非常必要的, 许多传统的阳极材料如不锈钢网、镁网、锌合金材料等可以有效阻止钝化钢筋的锈蚀^[14], 但是金属阳极材料面临着铺设

操作困难、经济性差、易腐蚀以及长期耐久性差等问题, 从而非金属复合材料尤其是导电水泥基材料作为阳极材料具有非常大的应用前景, 导电水泥基材料制备难度低、成本低、可适应不同的混凝土表面并且具有可重复使用的可能性。

水泥基材料尤其是混凝土材料具有高电阻的特点, 干燥的普通混凝土电阻率为 $6.5 \times 10^5 \sim 11.4 \times 10^5 \Omega \cdot \text{cm}$, 而碳质材料如炭黑、碳纤维(CF)、碳纳米纤维(CNF)、碳纳米管、石墨等可以提高水泥基材料的导电性能^[15-19]。张滇军等^[20]研究认为碳纤维导电砂浆与碳纤维导电混凝土的导电性能随龄期增长而显著变化。Sassani 等^[18]研究了碳纤维长度、掺量对导电混凝土电阻率与力学性能的影响, 得到结论为电阻随着碳纤维掺量的增加而降低, 且纤维长度对电阻影响并不显著。Walaszkowski 等^[21-22]制备了一种导电复合材料用作阳极, 该材料采用石墨作为导电成分, 聚合物作为基体, 在 ICCP 试验后发现, 阳极材料中石墨的含量为 40%~45%时, 保护效果较好。Canon 等^[23]在水泥净浆中掺入石墨, 制备出有效防护作

收稿日期: 2023-07-26。 修订日期: 2023-08-15。

基金项目: 国家自然科学基金(U2106220); 黑龙江省自然科学基金重点项目(ZD2021E007)。

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Received date: 2023-07-26. Revised date: 2023-08-15.

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用的水泥基复合阳极材料。为了满足实际应用，阳极材料的力学性能和长期耐久性也是亟需面对的问题，碳纤维作为主要导电介质的水泥基复合材料表现出优异的力学性能，尤其抗拉和抗弯性能突出，并且能够减少由于干燥引起的体积收缩问题。此外，该材料具有耐腐蚀的特点，能够抵御化学物质和环境因素的侵蚀^[24]。

本研究提出的高强低渗透水泥基阳极材料兼具表面防护和导电阳极功能，在实际工程应用凭借这种材料的低渗透性就可以物理阻挡外部有害离子的侵入；经过长时间服役后，当外部有害离子穿过表面防护层对钢筋锈蚀产生威胁时，可以启动 ICCP 对钢筋进行保护。综上所述，为了制备兼具优异力学性能、高导电性以及耐久性的阳极材料，提出了 2 种阳极材料：一种为以碳纤维、碳纳米纤维为主要导电介质的高强度碳纤维导电砂浆；另一种为内嵌碳纤维网格布的碳纤维导电砂浆，验证了 2 种阳极材料在 ICCP 方法中对钢筋保护的有效性，并对阳极材料在通电后的劣化规

律进行研究。

1 实验

1.1 制备

制备的 2 种阳极材料分别为由碳纤维(CF)与碳纳米纤维(CNF)混杂的碳纤维导电砂浆与内嵌碳纤维网格布的碳纤维导电砂浆，养护方式为 90 ℃ 蒸汽养护 3 d。

砂浆基体的胶凝材料由 P.O 42.5 水泥与硅灰组成，化学组成见表 1。2 种石英砂的粒径范围分别为 0.11~0.21 mm 与 0.21~0.38 mm，使用了聚羧酸高性能减水剂。碳纤维、碳纳米纤维以及碳纤维网格布的性能参数如表 2、3~表 4 所示。

表 1 胶凝材料的化学组成

Table 1 Chemical composition of cementitious materials w/%							
Material	CaO	SiO ₂	Al ₂ O ₃	MgO	SO ₃	Fe ₂ O ₃	R ₂ O
Cement	62.31	21.05	5.50	1.72	2.66	3.92	0.47
Silica fume	0.63	87.67	0.28	3.41	0.84	0.60	5.42

R₂O is oxides of elements like K and Na; w is mass fraction.

表 2 碳纤维性能

Table 2 Properties of carbon fiber

w(Carbon)/%	Tensile strength/MPa	Tensile modulus/GPa	Density/(g·cm ⁻³)	Resistivity/(Ω·cm)	Fiber diameter/μm	Length/mm
95	3 500	227	1.75	1.0–1.6	7	6

表 3 碳纳米纤维性能

Table 3 Properties of carbon nanofiber

Purity/%	Diameter/nm	Length/μm	Specific surface area/(m ² ·g ⁻¹)	Production method
>99.9	50–300	5–15	15–30	CVD method

CVD is chemical vapor deposition.

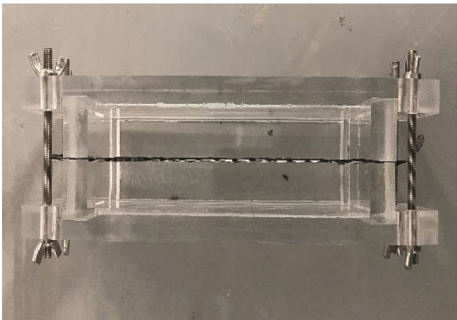
表 4 碳纤维网格布性能

Table 4 Properties of carbon fiber net cloth

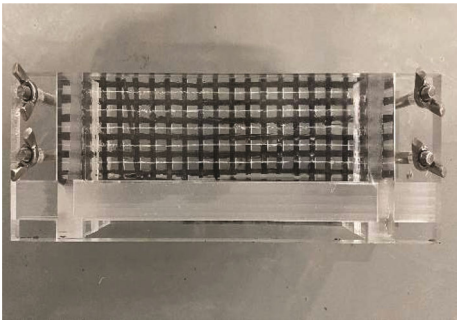
Tensile strength/MPa		Tensile modulus of elasticity/GPa		Elongation at break/%	
Vertical	Horizontal	Vertical	Horizontal	Vertical	Horizontal
2 580	3 160	219	310	1.2	1.3

砂浆基体的配合比见表 5。碳纤维导电砂浆中碳纤维(体积掺量为 0、1.0%、1.5%、2.0%)、碳纳米纤维(体积掺量为 0、0.6%、0.9%、1.2%)混杂，

砂浆基体的纤维组成如表 6 所示。碳纤维网格布层数为单层，其网格尺寸为 5 mm，垂直于试件表面放置，内嵌单层碳纤维网格布试件模具如图 1 所示。



(a) Top view



(b) Front view

图 1 内嵌单层碳纤维网格布模具

Fig. 1 Mold with embedded single-layer carbon fiber net cloth

表 5 砂浆基体的配合比
Table 5 Mortar matrix mix ratio

Water/binder ratio	Mix proportion/(kg·cm ⁻³)				w(SP) (by mass of binder)/%
	Cement	Silica fume	0.11–0.21 mm sand	0.21–0.38 mm sand	
0.26	920	276	202	810	2.30

表 6 砂浆基体的纤维掺量
Table 6 Fiber mixing of the anode material mortar matrix

Mortar No.	φ (CF)	φ (CNF)
CF0.0+CF0.0	0	0
CF1.0+CF0.6	1.0%	0.6%
CF1.5+CF0.6	1.5%	0.6%
CF2.0+CF0.6	2.0%	0.6%
CF1.0+CF0.9	1.0%	0.9%
CF1.5+CF0.9	1.5%	0.9%
CF2.0+CF0.9	2.0%	0.9%
CF1.0+CF1.2	1.0%	1.2%
CF1.5+CF1.2	1.5%	1.2%
CF2.0+CF1.2	2.0%	1.2%

φ is volume fraction.

表 7 混凝土配合比
Table 7 Concrete mix ratio

Water/binder ratio	Mix proportion/(kg·cm ⁻³)			w(NaCl) (by mass of water)/%	w(SP) (by mass of binder)/%
	Cement	Sand	Stone		
0.40	445	554	1233	3.5	0.4

1.2 力学性能测试

按标准 GB/T 17671—2021《水泥胶砂强度检验方法(ISO 法)》测试 2 种材料的力学性能^[25], 试件尺寸为 40 mm×40 mm×160 mm, 每个试验组测试 3 个试块, 计算平均值得抗弯强度与抗压强度。

1.3 电阻率测试

采用二电极法中的埋入法测试碳纤维导电砂浆的电阻, 试件尺寸为 40 mm×40 mm×40 mm, 将铁丝网埋入浆体中成型, 用数字电桥仪测试其电阻。

内嵌碳纤维网格布的碳纤维导电砂浆的电阻通过试件两侧伸出碳纤维网格布连导线接通数字电桥仪测试。

需要对试件进行蒸汽养护前(0 d)以及养护不同天数(1、2 d 和 3 d)的电阻率进行测试(自然冷却 24 h 后), 测试其电阻后计算电阻率, 公式如式(1)所示。

$$\rho = RS / L \quad (1)$$

式中: ρ 为材料电阻率, $\Omega \cdot \text{cm}$; R 为材料电阻值, Ω ; S 为试件横截面积, mm^2 ; L 为电极间距, mm 。

1.4 气体渗透性测试

圆柱体试件直径 50 mm、高度 25 mm。在蒸汽养护 3 d 后冷却至室温, 于侧面均匀涂抹环氧树脂

在 ICCP 加速试验中, 需要制备预留凹槽的钢筋混凝土构件, 后续试验中在凹槽中嵌入立方体海绵, 构件尺寸为 150 mm×150 mm×300 mm, 钢筋放置于混凝土构件中部位置。

混凝土试块 28 d 标准养护实测抗压强度为 42.9 MPa。配合比如表 7 所示, 为了模拟海洋环境中服役的钢筋混凝土构件, 在混凝土内部制造氯盐腐蚀环境, 在混凝土基体中引入了拌合水质量 3.5%的分析纯氯化钠, 细骨料为粒径小于 4.75 mm 的河砂, 其细度模数为 2.5, 碎石的粒径范围 4.75~20.00 mm, 钢筋混凝土构件养护方式为标准养护, 养护时间 28 d。

进行封闭处理。60 °C 烘干至质量不再改变后, 进行气体渗透性试验, 使用氮气作为渗透气体^[26–27]。

Klinkenberg 效应涉及渗透系数 K_v 的概念, 如式(2)^[28–29]:

$$K_a = K_v \left(1 + \frac{\beta_K}{p_m} \right) \quad (2)$$

式中: K_a 为表观气体渗透率, m^2 ; K_v 为本征气体渗透率, m^2 ; β_K 为 Klinkenberg 系数; p_m 为平均气体压力, bar。

通过对表观气体渗透率进行线性拟合, 图像截距代表了砂浆试件的本征气体渗透率。

1.5 单面吸水测试

完整试件即可应用于单面吸水测试, 试验方法参考 EN 13057^[30], 测试了完成气体渗透性试验的材料试件以及 ICCP 加速试验后的阳极材料试件。

试件底面与水面充分接触, 水深 5 mm, 在时间 $t=n^2$ ($n=0、2、3、4、5、6、7、8、9、10、11 \text{ min}$) 时将试件表面擦干后的记录质量变化, 计算单位表面积吸水体积 V_w , 线性关系如式(3), 通过斜率得到表面毛细吸水速率, 从而判断试件的抗渗性:

$$V_w = S\sqrt{t} + b \quad (3)$$

式中: V_w 为单位表面积吸水体积, mm; S 为表面毛细吸水速率, $\text{mm}/\text{min}^{0.5}$; t 为不同时刻, min; b 为拟合系数, mm。

1.6 阴极保护加速试验

通过阴极保护加速试验测试阳极材料在电流作用下性能劣化程度。在实际工程应用中, 外加电流的密度设计为 $20 \text{ mA}/\text{m}^2$, 扩大电流密度至 100 倍 ($2\,000 \text{ mA}/\text{m}^2$) 与 150 倍 ($3\,000 \text{ mA}/\text{m}^2$) 进行加速试验, 根据式(4)计算通电时间^[31–32]。

$$Q_{\text{实际}} = Q_{\text{试验}} = i_a \cdot t \quad (4)$$

式中: $Q_{\text{实际}}$ 为设计累积电荷密度, $\text{mA} \cdot \text{d}/\text{m}^2$; $Q_{\text{试验}}$ 为 ICCP 加速试验累积电荷密度, $\text{mA} \cdot \text{d}/\text{m}^2$; i_a 为钢筋表面电流密度, mA/m^2 ; T 为通电时长, d。

为了降低阳极材料与混凝土表面的接触电阻, 将海绵置于钢筋混凝土构件的预留凹槽中, 阳极材料置于混凝土构件下部, 与海绵表面充分接触, 保证电连续性, 连接方式示意图如图 5 所示, 利用导

线和直流电源将钢筋混凝土构件(钢筋作为阴极)与所制备的阳极材料进行连接, 各试验组的 ICCP 加速试验条件如表 8 所示, 对照组为未通电组, 仅浸泡于海水中, 试件浸泡在海水中, 模拟海水溶液按标准 ASTM D1141—1998(2021)《替代海水制备的标准规程》^[33]配制, 配比如表 9。

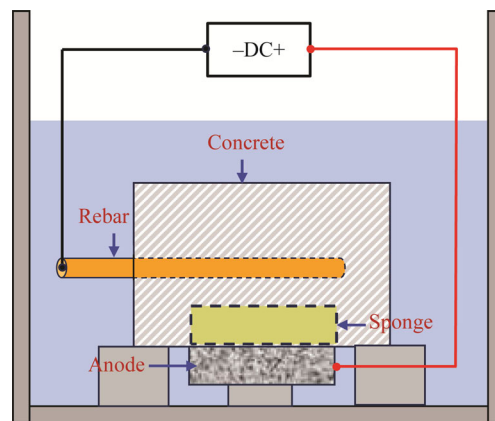


图 2 ICCP 试验电路连接示意图

Fig. 2 Schematic diagram of the circuit connection in ICCP accelerated test

表 8 ICCP 加速试验设计

Table 8 ICCP accelerated test design

Sample No.	Simulated ICCP energized time duration/a	Current density in the test/($\text{mA} \cdot \text{m}^{-2}$)	Duration of energization/d
Unenergized			
$2\,000 \text{ mA}/\text{m}^2$ (5 a)	5	2 000	18
$3\,000 \text{ mA}/\text{m}^2$ (5 a)	5	3 000	12
$2\,000 \text{ mA}/\text{m}^2$ (10 a)	10	2 000	36
$3\,000 \text{ mA}/\text{m}^2$ (10 a)	10	3 000	24

表 9 模拟海水溶液配比

Table 9 Simulated seawater solution preparation g/L

NaCl	MgCl ₂	Na ₂ SO ₄	CaCl ₂	KCl	NaHCO ₃
24.53	5.20	4.09	1.16	0.695	0.20

通过 ASTM C876《混凝土中无涂层钢筋腐蚀电位的标准试验方法》^[34]方法来确定钢筋的腐蚀状态并判断阳极材料在阴极保护试验中的有效性。在钢筋已经出现了初步的腐蚀情况后, 为钢筋施加 $100 \text{ mA}/\text{m}^2$ 的电流, 7 d 后测量钢筋瞬时关闭电位^[31, 35]。

对 ICCP 加速试验后阳极材料的微观形貌进行扫描电子显微镜(VEGA3 TESCAN)拍摄, 加速电压为 30.0 kV 。

2 结果与讨论

2.1 碳纤维导电砂浆

2.1.1 力学性能 掺入 CF 与 CNF 能够一定程度提高碳纤维导电砂浆基体的力学性能。图 3 为各实

验组的抗压强度与抗弯强度。图 4 为三点弯曲试验的荷载–位移曲线。所有试验组均为脆性断裂, 说明 CF 与 CNF 只能桥接微裂纹, 无法桥接宏观裂纹。根据试验结果, 可以发现抗压强度最高可提高 28%, 抗弯强度最高提高了 66%, 均是在碳纤维 1.0%+碳纳米纤维 0.6%复掺时。

CF 与基体之间存在一定的结合作用, 可以显著改善弯曲强度并提高材料的韧性^[36–37], 但由于 CF 表面疏水且呈现惰性, 与水泥水化产物之间缺乏物理粘附和化学粘附作用^[38], 减弱了对强度的增强作用。力学性能的提高依赖于 CNF 的作用, 纳米材料具有成核效应与填充效应, CNF 在早期水化过程中为水化产物的形成和生长提供成核位点, 细化了材料内部的孔结构, 降低了基体的总孔隙率, 并引入细小孔隙^[39–40], 此外, 碳纳米纤维会在胶凝材料中产生桥接效应^[41–42], 综合以上 2 种作用机理, CNF 提高了砂浆的力学性能。

纤维掺量再增加时, 产生力学性能倒缩的现象,

在纤维掺量最大(2%碳纤维+1.2%碳纳米纤维)时,力学性能最差,相比于强度最高组,抗压强度与抗弯强度分别降低了 15%与 19%,这是因为纤维在水泥浆体中的分散性会随着纤维掺量增加而变差。纤维掺量的增加还会大幅度降低浆体的流动性,此外,大掺量纤维之间互相搭接与团簇,从而在成型时会在浆体中引入更多空气与缺陷,从而在硬化后产生大量有害孔隙及缺陷过多的薄弱区域,降低了该材料的力学性能。

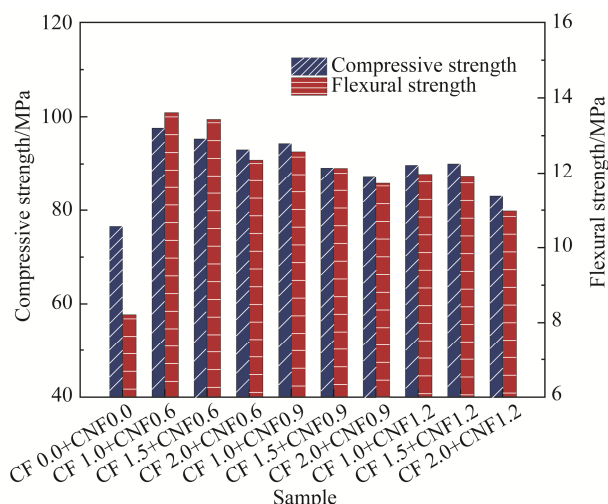


图3 碳纤维导电砂浆的力学性能

Fig. 3 Mechanical properties of carbon fiber conductive mortars

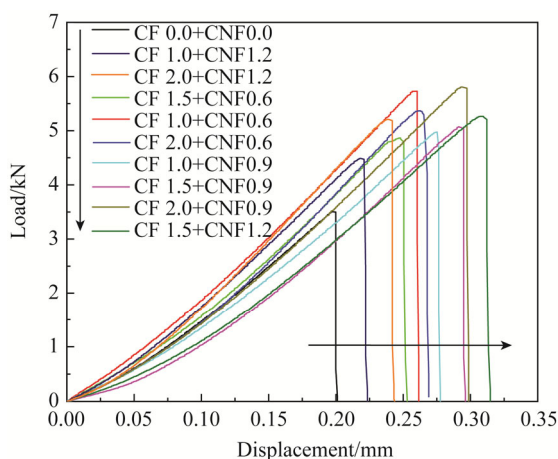


图4 碳纤维导电砂浆三点弯曲荷载-位移曲线

Fig. 4 Three-point bending load-displacement curve for carbon fiber conductive mortars

2.1.2 导电性能 各试验组的电阻率的变化情况表现出相似的趋势(见图 5): 当试件脱模后蒸汽养护 1 d 时, 电阻率大幅度增加; 而在蒸汽养护 1 d 后电阻率变化不明显。出现这种现象的原因是蒸汽养护过程提高了水化反应速率。而水泥基材料的导电作用依赖于孔溶液的电导率以及基体的孔隙率, 在蒸

养 1 d 后试件内部水化反应不再剧烈, 内部结构不再发生显著变化。

随着 CF 与 CNF 的掺入, 碳纤维导电砂浆材料的电阻率显著下降。通过分析蒸养 3 d 电阻率数据, 纤维掺量最高组(2.0%碳纤维+1.2%碳纳米纤维)的电阻率为 $160 \Omega \cdot \text{cm}$, 电阻率降低至未掺纤维试验组的近万分之一。当纤维掺量增加时, 砂浆试件内部形成了由 CF 和 CNF 相互连接而形成的导电网络。这种导电网络的完善程度增加, 电子的传导路径变得更畅通, 因此试件的导电性能也相应提高^[43]。但当纤维掺量增加到一定数量时, 在渗流阈值处已经构建了完善的导电通路, 电阻率不再明显下降。

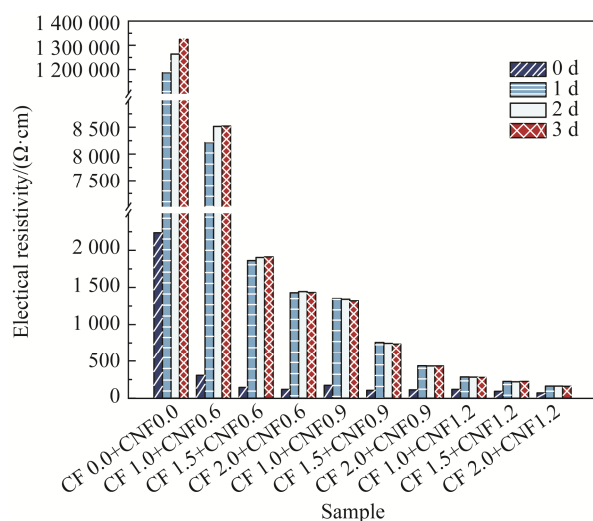


图5 不同养护时间各组碳纤维导电砂浆电阻率

Fig. 5 Resistivity of carbon fiber conductive mortars for each group with different curing time

2.1.3 抗渗性能 材料应用于海洋环境中, 兼具物理防护功能需要具有抵御海水中有毒离子的能力, 即具有优异的抗渗性, 气体渗透性试验(通过本征气体渗透率 K_v 表征)与单面吸水试验(通过表面毛细吸水速率 S 表征)可以表征抗渗性。

图 6 为气体渗透试验拟合结果。不同组别的碳纤维导电砂浆试件显示出类似的 K_v , 在 $0.16 \times 10^{-17} \text{ m}^2$ 到 $0.28 \times 10^{-17} \text{ m}^2$ 范围内变化。相比之下, 普通混凝土的 K_v 的数值范围在 $1 \times 10^{-17} \text{ m}^2$ 到 $1 \times 10^{-15} \text{ m}^2$ 之间。各组砂浆试件表面的毛细吸水速率线性拟合图像及数据如图 7 所示, 该材料的 S 在 $0.007 \text{ mm/min}^{0.5}$ 至 $0.01 \text{ mm/min}^{0.5}$ 之间变化, 表面毛细吸水速率为普通混凝土的 10% 左右, 对海工结构具有优异的物理防护功能。

2.2 内嵌碳纤维网格布的碳纤维导电砂浆

碳纤维网格布是使用碳纤维编织而成的, 它不仅具备出色的导电性能, 而且在力学性能方面表现

优异。综合碳纤维导电砂浆的性能,本节中选择力学性能与导电性能均表现优异的4组掺量(碳纤维:1.0%、1.5%;碳纳米纤维:0.6%、0.9%)作为内嵌碳纤维网格布的碳纤维导电砂浆基体配比。

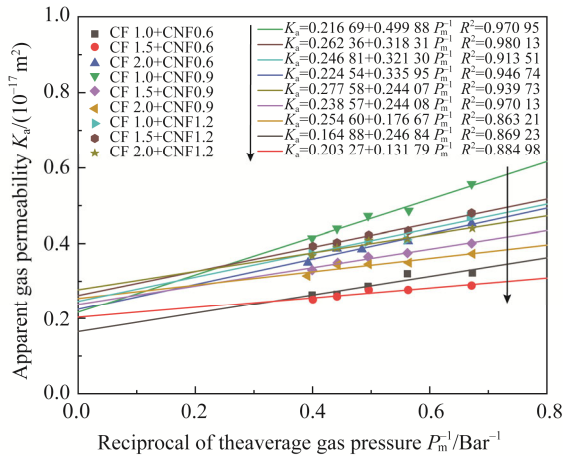


图6 碳纤维导电砂浆的气体渗透试验拟合结果

Fig. 6 Linear fitting results for gas permeation tests of carbon fiber conductive mortars

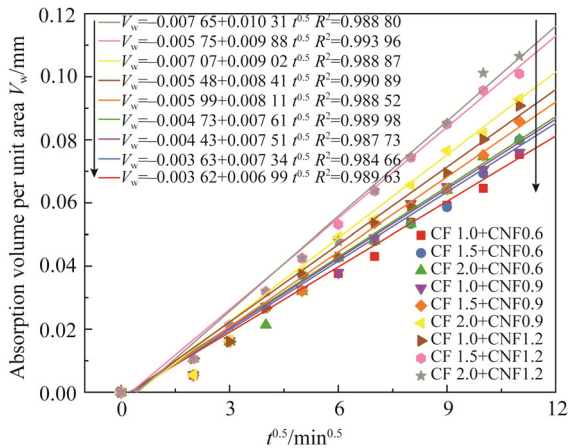


图7 碳纤维导电砂浆表面毛细吸水速率线性拟合图像

Fig. 7 Linearly fitted image of capillary water absorption rate on the surface of carbon fiber conductive mortars

2.2.1 力学性能 内嵌碳纤维网格布的碳纤维导电砂浆(本节简称:复合砂浆)力学性能及三点弯曲荷载-位移曲线分别如图8、图9所示。力学性能仍然呈现随着纤维掺量增强而降低的趋势,在内嵌碳纤维网格布的基础上,大量CF与CNF的引入会降低流动性,从而也会使碳纤维网格布与砂浆基体的界面变薄弱。

与未引入碳纤维网格布的碳纤维导电砂浆相比,本组复合砂浆材料的力学性能有一定程度的提升。如在碳纤维1%+碳纳米纤维0.6%复掺时,未内嵌碳纤维网格布时抗压强度与抗弯强度为97.6 MPa与13.6 MPa,内嵌碳纤维网格布后抗压强度与抗弯

强度提升至103.0 MPa与14.6 MPa,分别提高了5.5%与7.4%,说明碳纤维网格布的引入一定程度上提高了材料的力学性能。这是由于一层碳纤维网格布在基体中固定分布,约束了材料的开裂过程,提升了力学性能,尤其当碳纤维网格布承受弯曲荷载时能够充分发挥其抗拉强度。

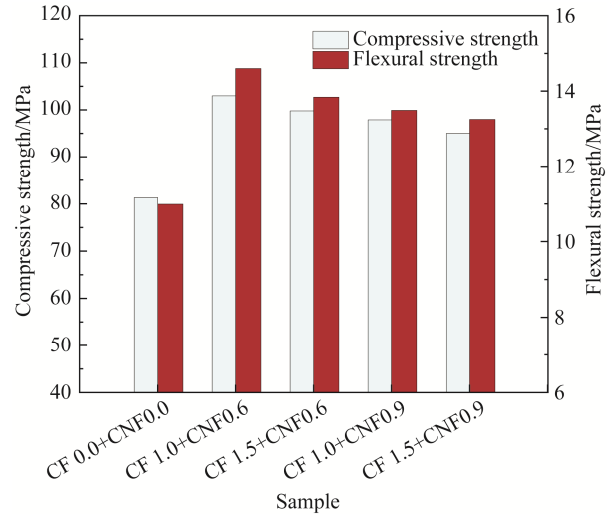


图8 复合砂浆的力学性能

Fig. 8 Mechanical properties of composite mortars

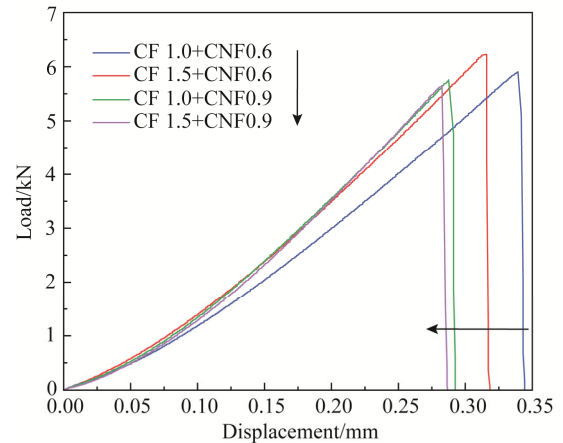


图9 复合砂浆的三点弯曲荷载-位移曲线

Fig. 9 Three-point bending load-displacement curves for composite mortars

2.2.2 导电性能 该复合砂浆材料的电阻率(如图10)仍然在蒸汽养护2 d至3 d后稳定,引入碳纤维网格布后,材料的电阻率随着导电纤维CF与CNF的掺量增加而降低。在1.5%碳纤维+0.9%碳纳米纤维复掺时,电阻率降至最低 $584 \Omega \cdot \text{cm}$,并且相比于同掺量下未内嵌碳纤维网格布的试验组($736 \Omega \cdot \text{cm}$)降低了21%。碳纤维网格布是由碳纤维编织而成,纤维之间的电流传导通路更为完整,碳纤维网格布与两种导电纤维CF、CNF协同作用,大幅度提高了复合砂浆材料的导电性能。

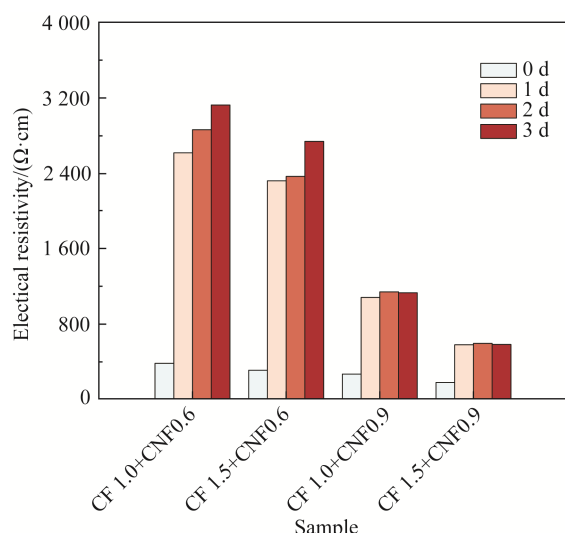


图 10 复合砂浆的电阻率

Fig. 10 Resistivity of composite mortars

2.2.3 抗渗性能 引入碳纤维网格布后, 复合砂浆材料的抗渗性测试结果分别如图 1、图 12 所示。该种复合砂浆材料的范围为 $0.08 \times 10^{-17} \text{ m}^2$ 至 $0.11 \times 10^{-17} \text{ m}^2$, S 范围为 $0.0066 \text{ mm/min}^{0.5}$ 至 $0.0840 \text{ mm/min}^{0.5}$ 之间, 并且仍然呈现了随着导电纤维体积掺量增加抗渗性下降的趋势。引入碳纤维网格布后, 复合砂浆的抗渗性略有提高, 这是由于碳纤维网格布具有高抗拉强度及弹性模量, 可以抑制收缩引起的裂纹的生长与扩展, 从而提高了材料的抗渗性。类似地, 本种材料也对海工结构具有优异的物理防护功能。

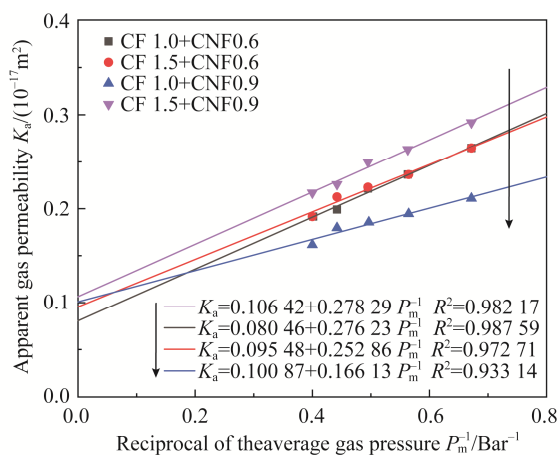


图 11 复合砂浆的气体渗透线性拟合图像

Fig. 11 Linearly fitted image of gas permeation of composite mortars

2.3 ICCP 加速试验对阳极材料性能劣化的影响

综合力学、导电、抗渗性能, 本试验条件下碳纤维导电砂浆最优掺量为 1.5% 碳纤维+1.2% 碳纳米纤维, 内嵌碳纤维网格布的碳纤维导电砂浆最优掺量为 1.5% 碳纤维+0.9% 碳纳米纤维。所以 ICCP 加

速试验中的阳极材料选择该 2 组材料作为阳极进行试验。

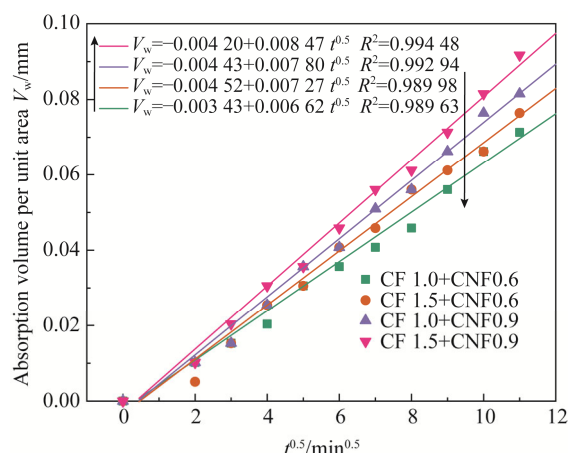


图 12 复合砂浆的单面吸水线性拟合结果

Fig. 12 Linear fitting results for one-sided water absorption of composite mortars

2.3.1 电化学电位测量 在对钢筋混凝土构件进行 ICCP 加速试验之前, 钢筋电位都大约在 -380 mV , 这意味着钢筋没有得到有效的保护, 并存在腐蚀现象, 这是由于氯离子导致了钢筋的腐蚀。瞬时关闭电位测量结果显示, 钢筋瞬时关闭电位约为 880 mV , 这也说明 ICCP 的有效性是显而易见的, 即证明制备的 2 种阳极材料在 ICCP 方法中的有效性, 通过施加外部电流, 成功地保护了钢筋。

2.3.2 力学性能 碳纤维导电砂浆阳极与内嵌碳纤维网格布的碳纤维导电砂浆阳极 ICCP 加速试验后的力学性能分别如图 13 与图 14 所示。与未使用的阳极材料的力学性能相比, 浸泡在海水中未通电的试验组的力学性能有略提高的现象, 这可能是浸泡在海水中基体发生了再水化现象, 从而强度提高^[44-46]。

当模拟 ICCP 通电时长为 5 a 且电流密度为 2000 mA/m^2 时, 相比于未通电试验组, 碳纤维导电砂浆阳极材料抗压强度与抗弯强度分别降低了 1.6% 与 3.7%, 内嵌碳纤维网格布的碳纤维导电砂浆阳极抗压强度与抗弯强度降低了 5.6% 与 3.9%; 当电流密度为 3000 mA/m^2 时, 碳纤维导电砂浆阳极材料抗压强度与抗弯强度降低了 4.5% 与 5.3%, 内嵌碳纤维网格布的碳纤维导电砂浆阳极材料抗压强度与抗弯强度降低了 8.9% 与 6.0%。

当模拟 ICCP 通电时长为 10 a 且电流密度为 2000 mA/m^2 时, 相比于未通电试验组, 碳纤维导电砂浆阳极材料抗压强度与抗弯强度降低了 7.2% 与 8.9%, 内嵌碳纤维网格布的碳纤维导电砂浆阳极抗

压强度与抗弯强度降低了 11.3%与 9.8%; 当电流密度为 $3\ 000\ \text{mA/m}^2$ 时, 抗压强度与抗弯强度降低了 9.6%与 11.9%, 内嵌碳纤维网格布的碳纤维导电砂浆阳极抗压强度与抗弯强度降低了 14.5%与 12.1%。

根据通电时长和电流密度的不同, 阳极材料通电后的力学性能发生了不同程度的轻微变化。随着通电时间和电流密度的增大, 阳极材料力学性能劣化程度变大。

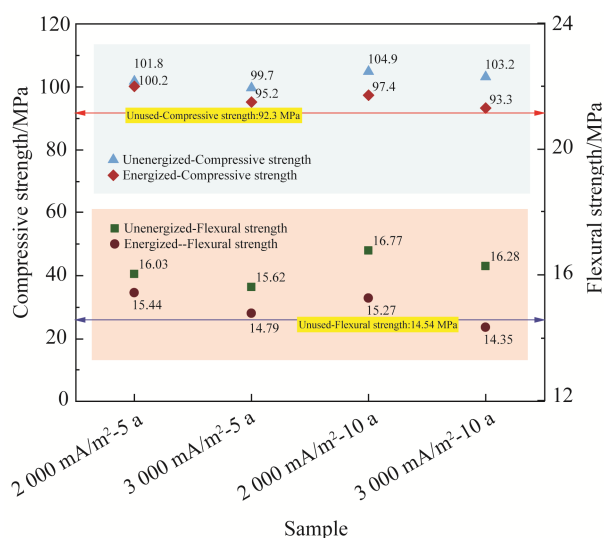


图 13 阴极保护加速试验前后碳纤维导电砂浆阳极材料力学性能(CF1.5+CNF1.2)

Fig. 13 Mechanical properties of carbon fiber conductive mortar anodes before and after ICCP accelerated test (CF1.5+CNF1.2)

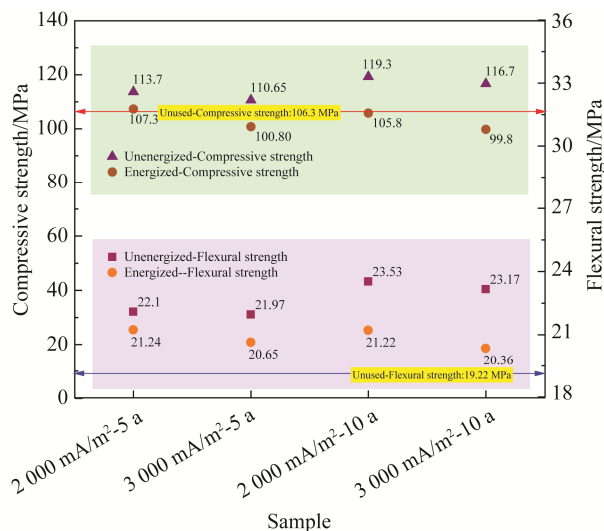


图 14 ICCP 加速试验前后内嵌碳纤维网格布的碳纤维导电砂浆阳极的力学性能(CF1.5+CNF0.9)

Fig. 14 Mechanical properties of carbon fiber conductive mortar anodes with embedded carbon fiber net cloth before and after ICCP accelerated test (CF1.5+CNF0.9)

2.3.3 导电性能 2 种阳极材料 ICCP 加速试验后的电阻率如图 15 所示, 通电后电阻率增大即导电

性能下降。并且当模拟 ICCP 通电时长为 10 a 并且电流密度为 $3\ 000\ \text{mA/m}^2$ 时导电性能下降最显著, 2 种阳极材料的电阻率分别提高了 11.6% 与 18.1%。说明导电介质(碳纤维、碳纳米纤维、碳纤维网格布)在通电后发生劣化, 导电通路受到破坏^[47]。

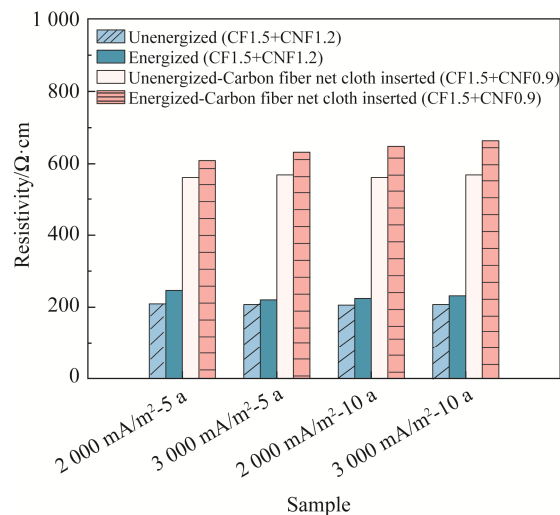


图 15 ICCP 加速试验前后阳极材料的电阻率

Fig. 15 Resistivity of anodes material before and after ICCP accelerated test

2.3.4 抗渗性能 电流密度为 $3\ 000\ \text{mA/m}^2$ 下, 不同通电时间条件下, 对进行 ICCP 加速试验后的阳极材料进行单面吸水测试, 2 种材料的试验结果分别如图 16 与图 17 所示。在模拟 ICCP 时长为 5 a 时, 相较于未通电的对照组, 通电后的 2 种阳极材料表面毛细吸水速率分别增加了 6.1%、降低了 1.3%。当模拟 ICCP 通电时长为 10 a 时, 2 种阳极材料的表面吸水速率分别增加了 12.5%与 1.4%, 这说明碳纤维导电砂浆抗渗性发生一定程度的劣化, 但内嵌碳纤维网格布的碳纤维导电砂浆阳极的抗渗性并没有发生明显变化, 这是因为碳纤维网格布在通电时承担了更大的电流作用, 从而保护了基体。

2.3.5 基体与碳纤维劣化前后微观形貌 对 $3\ 000\ \text{mA/m}^2-10\ \text{a}$ 试验组中阳极材料的微观形貌进行扫描电镜拍摄, 图 18 为基体通电前后微观形貌。由图 18 可见, 碳纤维导电砂浆阳极(简称: 导电砂浆阳极)材料的基体发生了很严重的劣化, 密度降低, 产生大量缺陷, 所以导致力学性能与抗渗性大幅度降低, 这是由于通电后会产生离子迁移、聚集等现象, 引起导电砂浆阳极基体内部产生化学反应, 从而使基体产生破坏、开裂等现象; 内嵌碳纤维网格布的碳纤维导电砂浆阳极(简称: 复合阳极)的基体微观形貌未发生显著差异, 这种现象也可以解释复合阳极抗渗性未明显降低的原因。

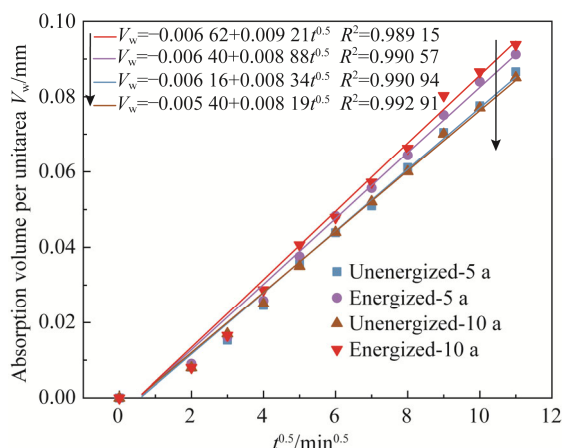


图 16 ICCP 前后碳纤维导电砂浆阳极材料的单面吸水试验结果(CF1.5+CNF1.2)

Fig. 16 One-sided water absorption test results of carbon fiber conductive mortar anodes before and after ICCP accelerated test (CF1.5+CNF1.2)

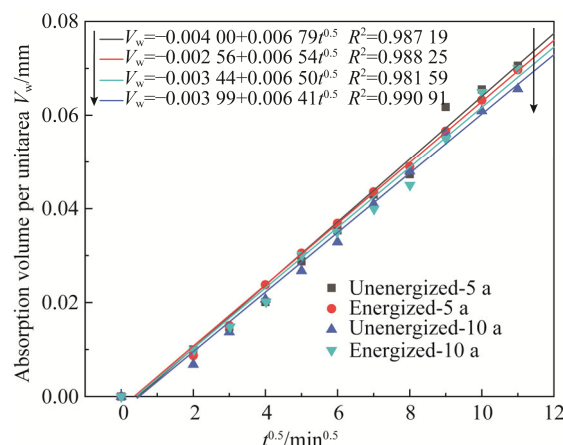
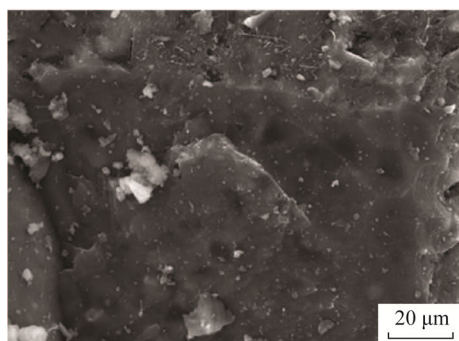
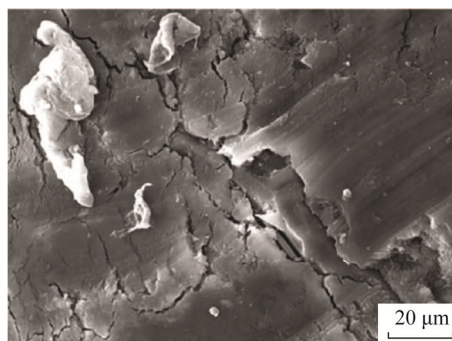


图 17 ICCP 试验前后内嵌碳纤维网格布的碳纤维导电砂浆阳极的单面吸水试验结果(CF1.5+CNF0.9)

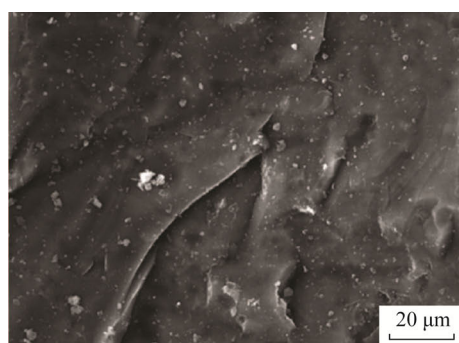
Fig. 17 One-sided water absorption test results of carbon fiber conductive mortar anodes with embedded carbon fiber net cloth before and after ICCP accelerated test (CF1.5+CNF0.9)



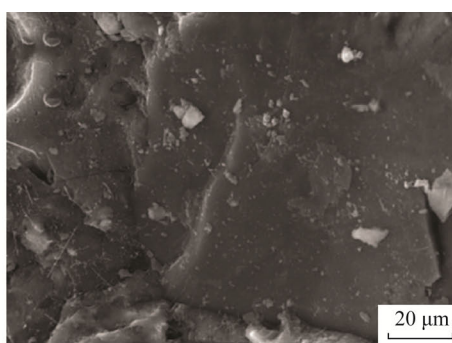
(a) Conductive mortar anode before energization



(b) Conductive mortar anode after energization



(c) Composite anode before energization



(d) Composite anode after energization

图 18 通电前后基体微观形貌照片

Fig. 18 Microscopic morphology images of matrix before and after energization

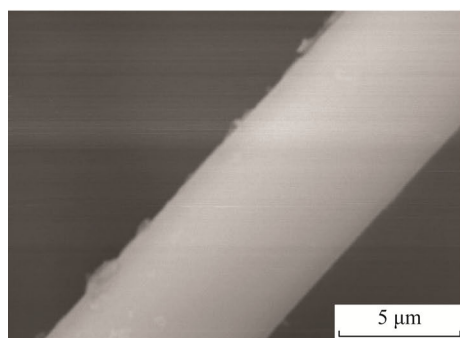
由于阴极保护过程中电流会对碳纤维的性能产生不利影响^[48], 通电时碳纤维与电解质溶液中的离子发生反应会产生电化学腐蚀, 而在电化学腐蚀过程中, 纤维表面成分会发生改变, 形成氧化物、酸或碱等化学物质, 原有结构发生破坏, 从而表面粗糙、脱落, 导致碳纤维的力学性能以及导电性能

降低。

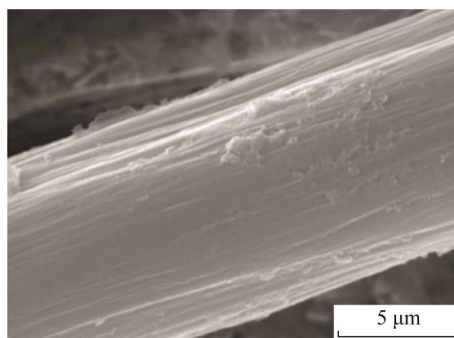
对通电前后的导电砂浆阳极材料基体中碳纤维、复合阳极内碳纤维网格布中的碳纤维进行扫描电镜拍摄(见图 19), 导电砂浆阳极材料基体中碳纤维通电后发生了一定程度的劣化, 所以 CF 与 CNF 在通电后导电搭接性能与对裂纹桥接性能降低, 从

而降低了力学性能与导电性能；碳纤维网格布中碳纤维发生了较为明显的破损，这也可解释为碳纤维

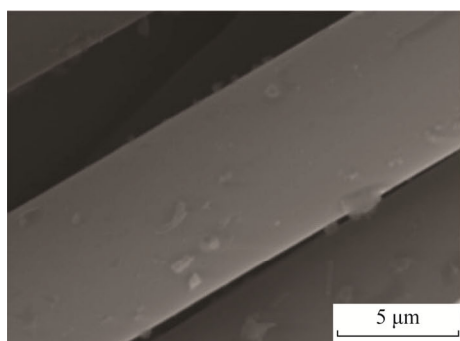
网格布起到主要导电作用，受到电流影响更严重，从而也保护了基体没有发生严重破坏。



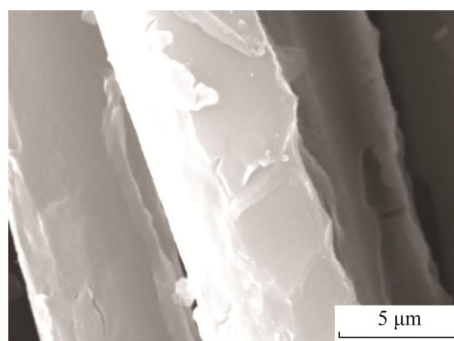
(a) Conductive mortar anode before energizing



(b) Conductive mortar anode after energization



(c) Composite anodes before energization
(Carbon fibers in carbon fiber net cloth)



(d) Composite anodes after energization
(Carbon fibers in carbon fiber net cloth)

图 19 通电前后碳纤维微观形貌照片

Fig. 19 Microscopic morphology images of carbon fiber before and after energization

3 结论

1) 碳纤维导电砂浆在 1.0%碳纤维+0.6%碳纳米纤维复掺时力学性能最佳，最大能够提高抗压强度 28%，抗弯强度 66%，随着纤维掺量增加力学性能有所降低；电阻率随着纤维掺量增加而显著降低，在 2.0%碳纤维+1.2%碳纳米纤维复掺时电阻率低至 $160 \Omega \cdot \text{cm}$ ；碳纤维导电砂浆材料具有很高的抗渗性，具有优异的物理防护功能。

2) 内嵌碳纤维网格布的碳纤维导电砂浆在碳纤维 1.0%碳纤维+0.6%碳纳米纤维复掺时抗压强度与抗弯强度分别达到 103.0 MPa 与 14.6 MPa；在 1.5%碳纤维+0.9%碳纳米纤维复掺时电阻率低至 $584 \Omega \cdot \text{cm}$ 。相比于碳纤维导电砂浆，力学性能、导电性能和抗渗性能均得到一定程度提升，说明碳纤维网格布与碳纤维、碳纳米纤维以及高强砂浆基体具有良好的协同作用。该种材料可作为重点构件的外加电流阴极保护的阳极，同时也可应用于高氯盐浓度环境的建筑构件电化学除氯。

3) 阴极保护加速试验证明了本研究中所制备阳极材料的有效性，通电后阳极材料的力学性能和导电性能发生了轻微劣化，抗压强度以及抗弯强度最大仅降低了 14.5%与 12.1%，电阻率最高增长了 18.1%。碳纤维导电砂浆阳极抗渗性降低，内嵌碳纤维网格布的碳纤维导电砂浆阳极材料的抗渗性未发生明显变化，碳纤维网格布承担主要的导电作用，保护了基体的完整性。

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Preparation and Properties of Cement-Based Anode Materials for Cathodic Protection Systems for Marine Engineering

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Extended Abstract

Introduction In the marine environment, reinforced concrete components are extremely vulnerable to corrosion by harmful ions in seawater, resulting in a serious damage. The impressed current cathodic protection method is one of the effective methods for corrosion protection of reinforced concrete structures. Conventional anode materials such as stainless-steel mesh, magnesium mesh and zinc alloy materials can effectively prevent the corrosion of passivated steel bars, but metal anode materials have some problems such as difficult laying operations, high-cost, susceptibility to corrosion and poor long-term durability. Thus, non-metallic composites, especially conductive cementitious materials can be used as promising anode materials. Conductive cementitious materials are simple to prepare, low-cost, adaptable to different concrete surfaces, and have a possibility of being reused. In this paper, a high-strength, low-permeability cement-based anode material was proposed due to its surface protection and conductive anode functions. Two kinds of cement-based anode materials were prepared in the laboratory, which were high-strength conductive mortar materials mixed with carbon fibers (CF) and carbon nanofibers (CNF) as well as conductive mortar materials embedded with carbon fiber net cloth, respectively. The mechanical properties, resistivity, and impermeability of the two anode materials were tested, and the evolution of the properties under the ICCP accelerated electric field was investigated.

Methods The cementitious material of the mortar matrix was composed of P.O 42.5 cement and silica fume, the particle sizes for two types of quartz sand were 0.11–0.21 mm and 0.21–0.38 mm, a high-performance polycarboxylate superplasticizer was used, and a water-binder ratio is 0.26. In the carbon fiber conductive mortar, carbon fibers (in volume fractions of 0%, 1.0%, 1.5%, 2.0%) and carbon nanofibers (in volume fractions of 0%, 0.6%, 0.9%, 1.2%) were mixed. The single layer carbon fiber net cloth with a mesh size of 5 mm and was placed vertically on the surface of the specimen. The anode materials were cured at 90 °C for 72 h.

The anode materials were subjected to the flexural and compressive strength tests (GB/T 17671—2021). Electrical resistivity tests (two-electrode method) were conducted on anode materials cured for different durations. Also, gas permeability tests and one-sided water absorption tests (EN 13057) were carried out to assess the permeability resistance of the anode materials. The performance degradation of the anode materials under the influence of electrical current was tested through cathodic protection acceleration experiments. The designed current density for external electrical current was 20 mA/m². Acceleration tests were conducted by increasing the current density to 100 times (*i.e.*, 2 000 mA/m²) and 150 times (*i.e.*, 3 000 mA/m²). The corrosion status of the rebar was determined by a model ASTM C876 standard test method to assess the effectiveness of the anode materials in the cathodic protection test. The microstructure of the anode materials after ICCP acceleration test at an acceleration voltage of 30.0 kV

was characterized by a model VEGA3 TESCAN scanning electron microscope.

Results and discussion For carbon fiber conductive mortar, the mixing of CF with CNF improves the mechanical properties and conductive properties of the carbon fiber conductive mortar matrix. The compressive strength and flexural strength of mortar with 1.0% CF + 0.6% CNF are increased by 28% and 66%, respectively. There is a binding effect between CF and matrix, which can significantly improve the bending strength and increase the toughness of the material, CNF has a nucleation effect and a filling effect, which refines the pore structure inside the material, and the bridging effect of CNF improves the mechanical properties of the material. The resistivity of the mortar fiber-doped with 2.0% CF + 1.2% CNF is $160 \Omega \cdot \text{cm}$, which is as low as nearly one ten-thousandth of that of the mortar fiber-undoped, this is a result of the formation of a conductive network inside the mortar specimen formed *via* the interconnection of CF and CNF.

For carbon fiber conductive mortar with embedded carbon fiber net cloth, the introduction of carbon fiber net cloth improves the mechanical properties of the material. This is due to the fixed distribution of a layer of carbon fiber net cloth in the matrix, which constrains the cracking process of the material. Carbon fiber mesh cloth is woven from carbon fibers. The current conduction path between the fibers is more complete. The introduction of carbon fiber net cloth, CF, and CNF improves the conductivity of the composite mortar materials.

Carbon fiber conductive mortar and carbon fiber conductive mortar with embedded carbon fiber net cloth both have superior impermeability properties. Intrinsic gas permeability K_v and capillary water absorption rate S are as low as one-tenth of ordinary concrete, indicating that the prepared anode material has a superior physical protection function.

The cathodic protection accelerated test proves the effectiveness of the anode material. The mechanical properties and electrical conductivity of the anode material after energized slightly deteriorates. The compressive and flexural strengths are decreased by only 14.5% and 12.1%, and the resistivity is increased by 18.1%. The anode impermeability of carbon fiber conductive mortar decreases. The impermeability of a conductive mortar embedded with carbon fiber mesh cloth and carbon fiber as an anode material does not change significantly because carbon fiber mesh cloth has a main conductive effect to protect the integrity of the substrate.

Conclusions The cement-based anode materials both had the superior mechanical properties, *i.e.*, the compressive and flexural strength of 103.0 MPa and 14.6 MPa, respectively, the resistivity of $160 \Omega \cdot \text{cm}$, the gas permeability and capillary water absorption rate of only 1/10 of the ordinary concrete. The concrete structure had a positive physical protection effect. After the ICCP acceleration, the mechanical properties and electrical conductivity of the two materials only produced a slight deterioration phenomenon, in which the anode material with carbon fiber net cloth performed more consistently. It could be suitable for cathodic protection of concrete with applied current. The cement-based anode materials can be also used for electrochemical chloride extraction of concrete components under high chloride salt environment conditions instead of the conventional anode materials.

Keywords marine concrete; impressed current cathodic protection; cement-based anode material; mechanical properties; electrical conductivity; impermeability